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(54) **Heat sink material for use with a semiconductor component and fabrication method thereof**

(57) A heat sink material for use with a semiconductor component having a coefficient of thermal expansion near to that of a semiconductor material and a high thermal conductivity, comprising a plurality of diamond particles, a metal, and a metal carbide, wherein the metal carbide and diamond particles constitute the matrix, and the metal fills the interstices of the matrix is provided. Also disclosed are a method for fabricating the same and a semiconductor package using the same.

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## Description

## Background of the Invention

## 5 Field of the Invention

The present invention relates to a heat sink material for releasing heat from a semiconductor component, and to a method for fabricating the same. The present invention also relates to a semiconductor device package or to a heat-release jig equipped with a heat sink formed of the inventive material

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## Background Art

Copper (Cu) is known as a typical material for use as a heat sink. However, although Cu has a relatively high thermal conductivity of 398 W/mK, the coefficient of thermal expansion is also large, having a value of 17 ppm/°C. Thus, when Cu is joined with a semiconductor, such as silicon (Si) having a coefficient of thermal expansion of 4.2 ppm/°C or gallium arsenide (GaAs) having a coefficient of thermal expansion of from 6 to 7 ppm/°C, both of the joined materials suffer a large thermal stress in the cooling process from the joining temperature to room temperature, or in the cooling process from the maximum temperature achieved during the operation of the semiconductor component to room temperature. In many cases, such a large thermal stress makes the component unfeasible for use. In the light of such circumstances, alloys of Cu with a material having small coefficient of thermal expansion (e.g., W (tungsten) or Mo (molybdenum)), such as CuW and CuMo are used. That is, design of a heat sink material which matches the semiconductor package is made possible by using a material whose coefficient of thermal expansion is controllable. In such cases, however, the alloy becomes inferior to Cu in terms of thermal conductivity, i.e., having a value of about 200 W/mK, because the metals (W or Mo) alloyed with Cu have small thermal conductivity.

25 Diamond has the highest thermal conductivity in the temperature range of from room temperature to the high temperature region of 200 °C. Moreover, the coefficient of thermal expansion thereof in the vicinity of room temperature is about 1.5 ppm/°C, which is smaller as compared with ordinary semiconductor materials such as Si and GaAs.

Therefore, it has been thought of using metallic materials containing particles of diamond embedded therein having such superior characteristics.

30 The idea of embedding diamond particles is disclosed in, for example, JP-A-Sho62-249462 (the term "JP-A-" as used herein signifies "an unexamined published Japanese patent application"), JP-A-Hei2-170452, JP-A-Hei3-9552, JP-A-Hei4-231436, JP-A-Hei4-259305, JP-A-Hei5-291444, and JP-A-Hei5-347370.

Disclosed in JP-A-Sho62-249462 is a material in which diamond is incorporated in a resin to improve thermal conductivity. However, since a resin generally is a poor conductor of heat, the thermal conductivity as a whole is not much improved.

35 Disclosed in JP-A-Hei2-170452, JP-A-Hei4-231436, JP-A-Hei4-259305, and JP-A-Hei5-347370 is disclosed a material comprising diamond particles embedded in a metallic matrix. Gold (Au), silver (Ag), copper (Cu), aluminum (Al), magnesium (Mg), etc., are used for the metallic matrix.

Also known (see H. L. Davidson et al., IEEE (1995), pp. 538) is a material based on diamond, which is prepared by 40 subjecting diamond to special coating with a metal, and then impregnating the resulting material with an alloy of Cu and Ag.

All of the cases described above comprises incorporating diamond particles into a metallic matrix. ~~That is,~~ the diamond particles are separated from each other with a metallic material interposed therebetween. Accordingly, heat should also be transferred by the metallic material, that is, by a material sequence ordered in the order of diamond/metal/diamond/metal/---. This structure is disadvantageous not only because thermal conductivity is impaired by the junction formed between diamond and the metallic material, but also because the sample itself cannot be shaped easily due to the weak bonding at the junction between diamond and the metallic material. In fact, the thermal conductivity achieved by a conventional heat sink was found to be 400 W/mK at best.

## 50 Summary of the Invention

Thus, an object of the present invention is to provide a heat sink for use with a semiconductor component, having a coefficient of thermal expansion well comparable to that of a semiconductor material and yet having high thermal conductivity.

55 Another object of the present invention is to provide a semiconductor device package which effectively releases heat upon its assembly and when the semiconductor component is in operation.

As a result of extensive study of the present inventors, it has been found that, by utilizing a material comprising a plurality of diamond particles previously connected with each other by a metal carbide and having an interstitial metal,

a heat sink for use with a semiconductor component having a coefficient of thermal expansion close to that of the semiconductor material and having an extremely high thermal conductivity can be obtained.

Thus, the heat sink material for use with a semiconductor component according to the present invention comprises a plurality of diamond particles, a metal, and a metal carbide, wherein the metal carbide and diamond particles constitute the matrix, and the metal fills the interstices of the matrix.

The phrase "material comprising a metal carbide and diamond particles constituting a matrix" as referred to herein signifies a "material comprising a plurality of diamond particles connected together by a metal carbide". More specifically, this material maintains the connected structure of diamond particles and metal carbide even when the metal of the heat sink is molten.

The basic concept of the present invention is that the diamond particles are not buried in metal, but that a metal carbide (or a metal carbide and graphite) is formed (grown) on the surface of the diamond particles to connect them together, which combination is then impregnated with a metal (Cu, Ag, Au, or Al). Briefly, the concept is more like a case of forming sintered diamond, and then incorporating an interstitial metal. The only difference is that the diamond particles themselves are not bonded together; thus, this material is different from sintered diamond.

Concerning the structure, the diamond particles are incorporated in the matrix of a metal carbide such as TiC, ZrC, or HfC, and a metal fills the interstices of the matrix comprising the diamond particles and the metal carbide. Thus, it can be seen that the structure of the heat sink for use with a semiconductor component according to the present invention greatly differs from the conventional one in which diamond particles are buried in a metal. More specifically, if metal is removed from a conventional heat sink material for a semiconductor component, the diamond particles become dis-united. In contrast to this, the diamond particles remain connected to each other in the heat sink according to the present invention.

In the conventional case, furthermore, a metal is always incorporated between each pair of diamond particles. Although there may partly be such a component in the heat sink of the present invention, many parts consist of a metal carbide alone. That is, many parts consist of only metal carbide incorporated between different diamond particles, and the metal carbide is in contact with the surfaces of the different diamond particles.

In such a material, heat is transferred by lattice vibration / electron / lattice vibration / electron---, it can be readily anticipated that a high thermal conductivity is achieved. Moreover, mechanical bonding strength is increased in such a case.

It is preferred to incorporate graphite in the matrix, because graphite may contribute to the improvement of thermal conductivity.

Preferably, the diamond particles have an average diameter of 60  $\mu\text{m}$  or larger, but not more than 700  $\mu\text{m}$ . If the diamond particles are less than 60  $\mu\text{m}$  in average diameter, the thermal conductivity tends to become too low; if the diamond particles exceed 700  $\mu\text{m}$  in average diameter, they lead to the generation of cracks in a semiconductor substrate when the heat sink is joined to the semiconductor component for use therewith. That is, when diamond particles having too large an average diameter are used, the in-plane distribution of the thermal expansion coefficient is found to greatly fluctuate so as to make it impossible for a thin semiconductor substrate to tolerate such a fluctuation. Thus, cracks are believed to form by such a mechanism.

The metal preferably is at least one selected from the group consisting of Ag, Cu, Au, and Al. The use of such a material makes it possible to achieve high thermal conductivity.

The metal carbide is at least one selected from the group consisting of TiC, ZrC, and HfC.

Preferably, metal carbides accounts for 5 % or less by volume of the entire body. If the volume fraction of the metal carbides exceeds 5 %, the amount of metallic component tends to become too large so as to deteriorate the thermal characteristics of the heat sink when used with a semiconductor component.

It is also preferred that the surface of the heat sink material is coated with a metal by means of plating or vapor deposition.

Furthermore, at least one of the insulators AlN and  $\text{Al}_2\text{O}_3$  is used for joining the surface of the heat sink with a semiconductor component.

The structures described above can be implemented by a method according to the present invention described below. A method for fabricating a heat sink for use with a semiconductor component according to the present invention comprises forming a metal carbide on the surface of diamond particles by filling a vessel with a plurality of diamond particles, and then bringing the outer surface of the diamond particles in contact with a molten first metal. Then, the interstices of the resulting sample are impregnated with a molten second metal.

Preferably, after the first metal alone is heated together with diamond particles to form a metal carbide, the remainder of the first metal is evaporated, and the second metal is heated to melting thereafter.

It is also preferred that the first metal comprises components having a melting point lower than that of the components constituting the second metal, such that only the first metal is molten to form the metal carbide when heating the first and the second metals at the same time with the diamond particles; and that, the second metal is allowed to melting thereafter.

Provided that the conditions allow the metal to undergo melting, the metal referred to in the above fabrication method may be molten in vacuum or under pressure. However, care should be taken that a large part (50 % or more) of diamond does not suffer degradation. That is, preferably, the process is performed at a temperature of 1,100 °C or lower. It is possible to carry out the process at a temperature of 1,100 °C or higher if the pressure is elevated to such a region under which the diamond phase remains stable; however, under such a condition, diamond particles undergo solid reaction with each other so as to be sintered. In such a case, the structure targeted by the present invention cannot be implemented.

In the semiconductor device package according to the present invention, the heat sink for use with a semiconductor component described above is brought into thermal contact with a semiconductor component, provided that the heat sink comprises a connection portion in which at least two diamond particles incorporated in the heat sink are arranged on the surface connecting the heat sink with the semiconductor component.

In this manner, a semiconductor package having excellent heat-releasing properties during assembling or upon operation of the semiconductor component can be realized.

#### Brief Description of the Drawings

FIG. 1 shows schematically a heat sink for use with a semiconductor component according to an embodiment of the present invention;

FIG. 2 shows schematically a first step of a method for fabricating a heat sink for use with a semiconductor component, according to an embodiment of the present invention;

FIG. 3 shows schematically a second step of a method for fabricating a heat sink for use with a semiconductor component, according to an embodiment of the present invention;

FIG. 4 shows schematically a third step of a method for fabricating a heat sink for use with a semiconductor component, according to an embodiment of the present invention;

FIG. 5 shows schematically a fourth step of a method for fabricating a heat sink for use with a semiconductor component, according to an embodiment of the present invention;

FIG. 6 shows schematically a fifth step of a method for fabricating a heat sink for use with a semiconductor component, according to an embodiment of the present invention;

FIG. 7 shows schematically a sixth step of a method for fabricating a heat sink for use with a semiconductor component, according to an embodiment of the present invention;

FIG. 8 shows schematically a first step of another method for fabricating a heat sink for use with a semiconductor component, according to another embodiment of the present invention;

FIG. 9 shows schematically a second step of another method for fabricating a heat sink for use with a semiconductor component, according to another embodiment of the present invention;

FIG. 10 shows schematically a third step of another method for fabricating a heat sink for use with a semiconductor component, according to another embodiment of the present invention;

FIG. 11 shows schematically a fourth step of another method for fabricating a heat sink for use with a semiconductor component, according to another embodiment of the present invention;

FIG. 12 shows schematically a fifth step of another method for fabricating a heat sink for use with a semiconductor component, according to another embodiment of the present invention;

FIGs. 13a and 13b schematically show first steps of a method for fabricating a heat sink for use with a semiconductor component according to Example 3 of the present invention, in which a different mold is used;

FIGs. 14a and 14b schematically show second steps of a method for fabricating a heat sink for use with a semiconductor component according to Example 3 of the present invention, in which a different mold is used;

FIGs. 15a and 15b schematically show third steps of a method for fabricating a heat sink for use with a semiconductor component according to Example 3 of the present invention, in which a different mold is used;

FIGs. 16a and 16b schematically show fourth steps of a method for fabricating a heat sink for use with a semiconductor component according to Example 3 of the present invention, in which a different mold is used;

FIGs. 17a and 17b schematically show fifth steps of a method for fabricating a heat sink for use with a semiconductor component according to Example 3 of the present invention, in which a different mold is used;

FIGs. 18a and 18b schematically show sixth steps of a method for fabricating a heat sink for use with a semiconductor component according to Example 3 of the present invention, in which a different mold is used; and

FIG. 19 shows schematically a perspective view of a heat sink for use with a semiconductor component according to the present invention, which is joined with a semiconductor component and enclosed in a device package.

#### Detailed Description of the Invention

An embodiment of the present invention is described in detail with reference to the attached drawings.

FIG. 1 shows schematically the constitution of a heat sink material for use with a semiconductor component according to an embodiment of the present invention. Referring to FIG. 1, a heat sink 10 for use with a semiconductor component according to an embodiment of the present invention comprises a plurality of diamond particles 1, a metal carbide 2, and a metal 3. The diamond particles 1 are isolated from each other. The metal carbide 2 is formed on the outer periphery of the isolated diamond particles 1 to connect the diamond particles 1 with each other. In this manner, the metal carbide 2 and the diamond particles 1 form a matrix. The metal 3 is present in the interstices of the matrix.

A method for fabricating the above heat sink material for use with a semiconductor component according to the present invention is described below.

FIG. 2 to FIG. 7 schematically show the fabrication steps of a heat sink material for use with a semiconductor component according to an embodiment of the present invention.

Referring to FIG. 2, diamond particles 1 are placed inside a vessel 5.

Referring next to FIG. 3, a metal 2a is provided in contact with diamond particles 1. The metal 2a comprises an alloy of, for instance, Ti (the metal component for a metal carbide) and at least one metal selected from the group consisting of Ag, Cu, Al, and Au. A preferable metal component other than Ti is Zr or Hf, but also usable are combinations of metals selected from Groups 4a to 7a of the periodic table. From the viewpoint of thermal characteristics, the amount of Ti is preferably small, but Ti incorporated in too small an amount is ineffective. Thus, the alloy 2a preferably contains from 0.1 to 8.0 % by weight of Ti.

Referring to FIG. 4, the metal 2a is made molten by heating. The molten metal 2b permeates the interstices of the diamond particles 1, and Ti incorporated in the molten metal 2b reacts with the diamond to form a metal carbide 2 comprising TiC on the surface of the diamond particles 1. Depending on the conditions, graphite (not shown) may be formed occasionally at the same time on heating. The graphite is obtained from the diamond.

More graphite tends to generate with elevating melting temperature of the metal 2a and with increasing the duration of the heating. The use of an alloy for the metal 2a, which is later made molten, is effective, because the melting point can be lowered so as to prevent damage from occurring to the diamond and to decrease the amount of graphite that is generated by the heating.

Graphite is inferior to diamond from the viewpoint of thermal conductivity; however, it sometimes functions effectively to bond the diamond particles. Moreover, the presence of graphite in small quantity is of no problem, because it does not greatly influence the thermal conductivity of the material as a whole.

The metal 2b can be evaporated by heating it in vacuum.

Referring to FIG. 5, it can be seen that only diamond 1 and metal carbide 2 remain after the metal 2b is evaporated. The resulting structure comprises diamond particles 1 embedded in the matrix of the metal carbide 2. Diamond 1 is present as particles, and the particles are not in contact. However, the diamond particles 1 formed by the method above are joined with each other by the metal carbide, and are prevented from disuniting. Interstitial spaces can be found to form in the matrix composed of diamond particles 1 and the metal carbide 2.

Referring next to FIG. 6, a metal 3a is in contact with the matrix comprising diamond particles 1 and the metal carbide 2. The metal 3a comprises at least one selected from the group consisting of Ag, Cu, Al, and Au. By melting the metal 3a, the metal 3a easily penetrates the interstices of the matrix comprising the diamond particles 1 and the metal carbide 2 so as to fill the interstices. For the metal 3a, which is molten and used for infiltration, an elemental metal is preferred because it has a high thermal conductivity. If an alloy comprising two or more types of metal is used, on the other hand, the interstices can be filled up more easily because of the lowered melting point. However, the use of an alloy is disadvantageous because it reduces the resultant thermal conductivity. Thus a heat sink material for use with a semiconductor component as shown in FIG. 7 is implemented.

In the heat sink material for use with a semiconductor component thus implemented, the diamond particles 1, the metal carbide 2, and the metal 3 are brought into tight contact with each other both thermally and mechanically, and they yield a coefficient of thermal expansion that is close to the value of a semiconductor material. Accordingly, the resulting material functions sufficiently as a heat sink material for use with a semiconductor component.

A heat sink material for use with a semiconductor component can be fabricated in accordance with another process.

FIGs. 8 to 12 schematically show the steps for fabricating a heat sink material for use with a semiconductor component according to another embodiment of the present invention. Referring to FIG. 8, diamond particles 1 are placed inside a vessel 5.

Referring next to FIG. 9, a metal 2a and a metal 3a are provided in contact with the diamond particles 1. The metal 2a comprises an alloy of, for instance, Ti (the metal component for a metal carbide) and at least one metal selected from the group consisting of Ag, Cu, Al, and Au. The metal 3a comprises an alloy containing at least one metal selected from the group consisting of Ag, Cu, Al, and Au, but free of Ti (the metal component for a metal carbide).

A preferable metal component for the metal carbide other than Ti is Zr or Hf, but also usable are combinations of metals selected from Groups 4a to 7a of the periodic table. From the viewpoint of thermal characteristics, the amount of Ti is preferably small, but Ti incorporated in too small an amount is ineffective. Thus, the alloy 2a preferably contains

from 0.1 to 8.0 % by weight of Ti.

Referring to FIG. 10, only metal 2a is melted by heating. The molten metal 2b permeates the interstices of the diamond particles 1, and Ti incorporated in the molten metal 2b reacts with diamond to form a metal carbide (TiC) 2 on the surface of the diamond particles 1. Depending on the conditions, graphite (not shown) may occasionally be formed at the same time upon heating. The graphite is obtained from diamond. More graphite tends to generate with elevation of the melting temperature of the metal 2a and with increasing duration of the heating.

Once metal 2a undergoes melting, the metal 3a in contact therewith also undergoes melting more easily. Even if the melting of metal 2a does not facilitate melting of metal 3a, the metal 3a can be melted by raising the temperature to the melting point of the metal 3a or higher. In this manner, the molten metal 3a infiltrates the interstices of the matrix comprising diamond particles 1 and the metal carbide 2.

Referring now to FIG. 11, by carrying out the two-step melting process for melting the metals 2a and 3a, a matrix is first formed by the diamond particles 1 and the metal carbide 2, and then, a structure comprising the metal 2a or 3a incorporated in the interstices of the matrix is formed. Thus there is obtained a heat sink material for use with a semiconductor component, as shown in FIG. 12.

In order to lower the melting point, the metal 2a is preferably an alloy. However, the use of an alloy is disadvantageous in one aspect because it impairs overall thermal conductivity. Thus, in the present method, pure metal is used preferentially for the metal 3a, so as to make it possible to maintain the thermal conductivity of the alloy comprising metals 2a and 3a at a sufficiently high level.

## EXAMPLES

The present invention is described in further detail below by making reference to Examples, but it should be noted that the present invention is not only limited thereto.

### EXAMPLE 1

Diamond particles 1 weighing 0.5 g and having an average diameter of from 10 to 700  $\mu\text{m}$  were charged into a quartz vessel 5 having a diameter of 10 mm and a height of about 10 mm (FIG. 2), and there after a block of metal containing from 0.2 to 2.0 g of an active silver solder 2a (containing Ag, Cu, and Ti at a ratio of Ag:Cu:Ti = 0.7:0.28:0.02) was mounted thereon (FIG. 3). The assemblage was then held within a temperature range of from about 900 to 1,100  $^{\circ}\text{C}$  in vacuum ( $10^{-5}$  Torr) for a duration of 3 to 10 minutes (FIG. 4). In this manner, the active silver solder 2a infiltrated the interstices of the diamond particles 1, and the residual molten metal 2b was evaporated to obtain a porous body comprising diamond particles 1 bonded together by TiC 2 to form a matrix (FIG. 5). Then, a block of Ag, Cu, or Al was mounted on the resulting porous body, and was allowed to melt in vacuum ( $10^{-5}$  Torr) by holding the temperature for a duration of 2 minutes at about 970, 1,100, or 800  $^{\circ}\text{C}$ , respectively. Thus, Ag, Cu, or Al was allowed to fill the pores (FIG. 6). Thus there were obtained samples 10, each comprising a porous body made from diamond particles 1 and TiC 2 and with the pores thereof being filled with Ag, Cu, or Al 3 (FIG. 7). Thermal conductivity of the thus obtained samples was measured, and the results are summarized in Tables 1 and 2.

TABLE 1

| Particle diameter of diamond ( $\mu\text{m}$ ) | Metal impregnated later | Thermal conductivity (W/mK) |
|------------------------------------------------|-------------------------|-----------------------------|
| 700                                            | Silver                  | 900                         |
| 300                                            | Silver                  | 880                         |
| 200                                            | Silver                  | 790                         |
| 100                                            | Silver                  | 630                         |
| 60                                             | Silver                  | 500                         |
| 10                                             | Silver                  | 350                         |
| 300                                            | Copper                  | 800                         |
| 300                                            | Aluminum                | 650                         |

TABLE 2

| Particle diameter of diamond ( $\mu\text{m}$ ) | Amount of diamond (g) | Amount of active silver solder (g) | Thermal conductivity (W/mK) |
|------------------------------------------------|-----------------------|------------------------------------|-----------------------------|
| 300                                            | 0.5                   | 2.0                                | 750                         |
| 300                                            | 0.5                   | 1.0                                | 830                         |
| 300                                            | 0.5                   | 0.5                                | 880                         |
| 300                                            | 0.5                   | 0.3                                | 900                         |
| 300                                            | 0.5                   | 0.2                                | Sample Unavailable          |
| 300                                            | 0.5                   | 0.1                                | Sample Unavailable          |
| 300                                            | 0.5                   | 0.0                                | Sample Unavailable          |

It can be seen from the above results that Ag, Cu, or Al functions effectively as a metal to be infiltrated into the structure, and that a thermal conductivity of 500 W/mK or higher is achieved by using such a metal. Furthermore, it has been found that diamond particles 60  $\mu\text{m}$  or larger in diameter are effective to yield a thermal conductivity of not higher than the infiltrated metal. It is also found that better characteristics are obtained by decreasing quantity of silver solder. However, silver solder has an important function to form TiC, because, when the quantity thereof becomes 0.3 g or less, it is difficult to form the desired material.

Although the coefficient of thermal expansion differs depending on the volume fraction of diamond, a value in a range of from 7 to 12 ppm/K on average is obtained for the temperature range from room temperature to 500 °C. This value for the coefficient of thermal expansion falls between those for a metal (from 16 to 20 ppm/K) and that of diamond (2 ppm/K).

#### EXAMPLE 2

Diamond particles 1 weighing 0.5 g and having an average diameter of from 10 to 700  $\mu\text{m}$  were charged into a quartz vessel 5 having a diameter of 10 mm and a height of about 10 mm (FIG. 8), and after mounting thereon a metal block containing from 0.2 to 2.0 g of an active silver solder 2a (containing Ag, Cu, and Ti at a ratio of Ag:Cu:Ti = 0.7:0.28:0.02) together with 0 to 2 g of Ag or Cu 3a (FIG. 9), the assemblage was held at a temperature of 930 °C in vacuum ( $10^{-5}$  Torr) for a duration of 1 to 3 minutes (FIG. 10). In this manner, the active silver solder 2a first infiltrated the interstices of the diamond particles 1. Then, the resulting structure was held at a temperature of 980 °C in vacuum ( $10^{-5}$  Torr) for a duration of 1 to 3 minutes. This time, Ag or Cu 3a was molten, and infiltrated the interstices of the structure (FIG. 11). Thus, TiC 2 was formed on the surface of diamond particles 1, and a sample 10 comprising Ag or Cu 3a incorporated into the pores of the resulting porous body formed by diamond particles 1 and TiC 2 was obtained (FIG. 12). In addition to TiC 2, graphite was also found to form under high temperature conditions. The thermal conductivity of the resulting sample was measured. Thus obtained results are shown in Tables 3 and 4.

TABLE 3

| Particle diameter of diamond ( $\mu\text{m}$ ) | Metal impregnated later | Thermal conductivity (W/mK) |
|------------------------------------------------|-------------------------|-----------------------------|
| 700                                            | Silver                  | 750                         |
| 300                                            | Silver                  | 710                         |
| 200                                            | Silver                  | 690                         |
| 100                                            | Silver                  | 600                         |
| 60                                             | Silver                  | 450                         |
| 10                                             | Silver                  | 300                         |

TABLE 4

| Particle diameter of diamond ( $\mu\text{m}$ ) | Amount of diamond (g) | Amount of active silver solder (g) | Amount of silver (g) | Thermal conductivity (W/mK) |
|------------------------------------------------|-----------------------|------------------------------------|----------------------|-----------------------------|
| 300                                            | 0.5                   | 2.0                                | 1.0                  | 590                         |
| 300                                            | 0.5                   | 1.0                                | 1.0                  | 650                         |
| 300                                            | 0.5                   | 0.5                                | 1.0                  | 700                         |
| 300                                            | 0.5                   | 0.3                                | 1.0                  | 750                         |
| 300                                            | 0.5                   | 0.2                                | 1.0                  | Sample Unavailable          |
| 300                                            | 0.5                   | 0.1                                | 1.0                  | Sample Unavailable          |
| 300                                            | 0.5                   | 0.0                                | 1.0                  | Sample Unavailable          |
| 300                                            | 0.5                   | 1.0                                | 0.0                  | 300                         |

It is seen from the results above that a different metal can be introduced together with an active silver solder, and that they can be molten separately and infiltrated; and that thereby specimens having a thermal conductivity of 450 W/mK or higher and comprising diamond particles 60  $\mu\text{m}$  or larger in diameter are obtainable. Furthermore, it has been found that better characteristics are obtained with decreasing the quantity of the active silver solder. However, silver solder has an important role to form TiC, because, when the quantity thereof becomes 0.2 g or less, it is difficult to form the material. Moreover, the thermal conductivity drops with increasing amount of the active silver solder. Accordingly, the incorporation of active silver solder alone is completely ineffective.

As was the case in Example 1, furthermore, the value for coefficient of thermal expansion in the temperature range of room temperature to 500 °C falls in a range of 7 to 12 ppm/K on average.

### EXAMPLE 3

In FIGs. 13a and 13b through FIGs. 18a and 18b there are schematically shown the process steps for producing heat sink for use with a semiconductor component according to Example 3 of the present invention. Cases using different molds are shown in parallel with each other.

Referring to FIGs. 13a and 13b, diamond particles 1 having an average diameter of 10 to 700  $\mu\text{m}$  were placed in each of quartz vessels 15a and 15b differing from each other in internal shape.

Referring to FIGs. 14a and 14b, an active silver solder block 2a was mounted on the diamond particles 1, and was melted by maintaining the resulting structure in the temperature range of about 900 to 1,100 °C in vacuum ( $10^{-5}$  Torr) for a duration of from 3 to 10 minutes.

In this manner, referring to FIGs. 15a and 15b, the molten active silver solder 2b infiltrated the interstices of the diamond particles 1, and after a metal carbide was formed through the reaction with the diamond particles 1, the residual molten metal 2b was allowed to evaporate.

Thus, referring to FIGs. 16a and 16b, porous bodies each comprising diamond particles 1 bonded by TiC 2 were obtained.

Referring to FIGs. 17a and 17b, thereafter, a metal block 3a comprising Ag, Cu, or Al was mounted on the resulting porous body, and was allowed to melt in vacuum ( $10^{-5}$  Torr) by holding the temperature at about 970, 1,100, or 800 °C for a duration of 2 minutes. Thus, the metal 3a was allowed to fill the pores. By using molds differing in shape, heat sinks for use with a semiconductor component and having relatively freely choosable shape were obtained as shown in FIGs. 18a and 18b.

### EXAMPLE 4

FIG. 19 is a schematically drawn perspective view showing the heat sink according to the present invention bonded with a semiconductor component and packaged. Referring to FIG. 19, a semiconductor component 30 containing Si or GaAs as the principal material is electrically contacted, the resulting structure is enclosed in a package 20, and the heat sink side 10 is brought into contact with a heat pipe 40. The semiconductor component 30 was operated in order to test for heat radiation. A fin was provided on the back of the heat sink 10 to release heat.

As a result, the thermal resistance was found to decrease by using the present invention as the heat sink 10 in the place of Cu. The results are summarized in TABLE 5.

TABLE 5

| Sample             | Temperature difference<br>for 10 W (°C) | Thermal resistance<br>(°C/W) |
|--------------------|-----------------------------------------|------------------------------|
| Cu                 | 73                                      | 7.3                          |
| No. (1) in TABLE 1 | 63                                      | 6.3                          |
| No. (2) in TABLE 1 | 50                                      | 5                            |

Furthermore, in the case where a metal solder is used to join the heat sink 10 with the semiconductor component 30, it is found necessary to incorporate 2 or more diamond particles in the bonding plane of the heat sink located under the semiconductor component 30.

As described above, the heat sink material for use with a semiconductor component according to the present invention has a coefficient of thermal expansion close to that of a semiconductor material and a high thermal conductivity. Accordingly, by embedding the heat sink according to the present invention into a semiconductor device package, the heat that is generated upon assembly of the device or during operation of the semiconductor component can be released efficiently.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

#### Claims

1. A heat sink material for use with a semiconductor component, comprising a plurality of diamond particles, a metal, and a metal carbide, wherein the metal carbide and diamond particles constitute a matrix, and the metal fills the interstices of the matrix.
2. The heat sink material as in Claim 1, further comprising graphite included in the matrix.
3. The heat sink material as in Claim 1, wherein the diamond particles have an average diameter from about 60  $\mu\text{m}$  to about 700  $\mu\text{m}$ .
4. The heat sink material as in Claim 1, wherein the metal is at least one selected from the group consisting of Ag, Cu, Au, and Al.
5. The heat sink material as in Claim 1, wherein the metal carbide is at least one selected from the group consisting of TiC, ZrC, and HfC.
6. The heat sink material as in Claim 1, wherein the metal carbide accounts for 5% or less by volume of the material.
7. The heat sink material as in Claim 1, wherein the surface of the material is coated with a metal by means of plating or vapor deposition.
8. The heat sink material as in Claim 1, wherein at least one insulator selected from the group consisting of diamond, AlN, and  $\text{Al}_2\text{O}_3$  is used to join the heat sink material to a semiconductor component.
9. A method for fabricating a heat sink material for use with a semiconductor component, comprising:
  - forming a metal carbide on the surface of diamond particles by filling a vessel with a plurality of diamond particles, and then contacting the outer surface of the diamond particles with a molten first metal; and
  - impregnating the interstices of the resulting material with a molten second metal.
10. The method according to Claim 9, wherein,
  - the metal carbide is formed by heating the first metal alone with the diamond particles, and after evaporating the remainder of the first metal, the second metal is heated to melting.

11. The method according to Claim 9, wherein,

the first metal comprises components having a melting point lower than that of the components constituting the second metal, such that:

only the first metal is molten to form the metal carbide by heating the first and the second metals at the same time with the diamond particles, and that the second metal is melted thereafter.

12. The method according to Claim 9, wherein,

the melting points of the first and the second metals are 1,100 °C or lower.

13. The method according to Claim 9, wherein,

the first and the second metals are molten under a pressure of 1,000 at or under vacuum.

14. A semiconductor package comprising a semiconductor component connected with a heat sink comprising the heat sink material of Claim 1, wherein the heat sink comprises a connection portion in which at least two diamond particles incorporated in the heat sink material are arranged on the surface connecting the heat sink with the semiconductor component.

Fig.1

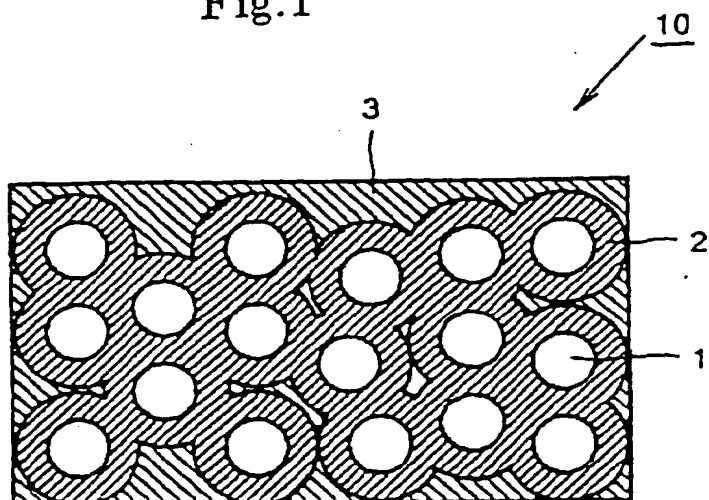


Fig.2

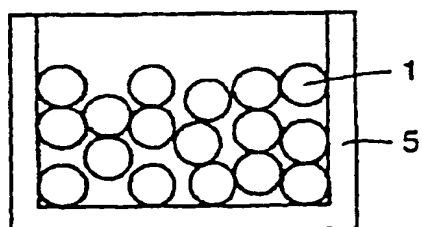


Fig.3

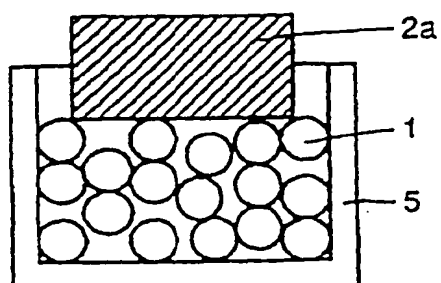


Fig.4

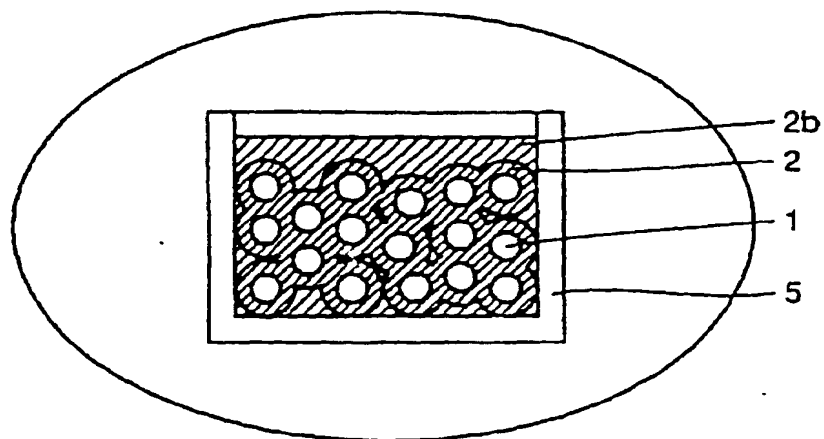


Fig.5

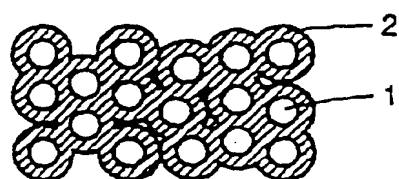


Fig.6

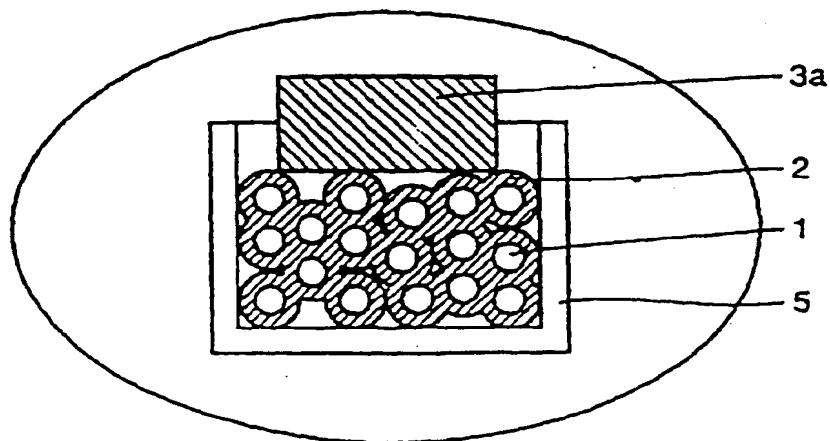


Fig.7

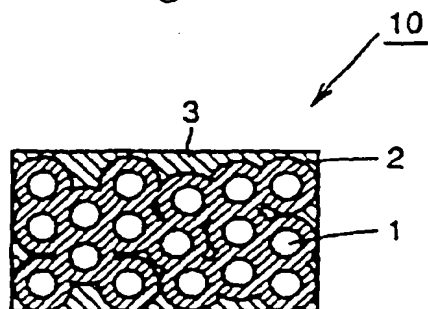


Fig.8

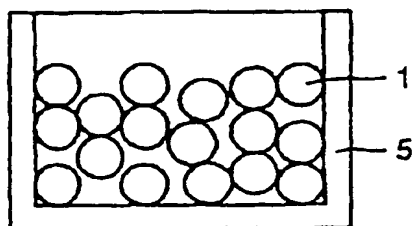


Fig.9

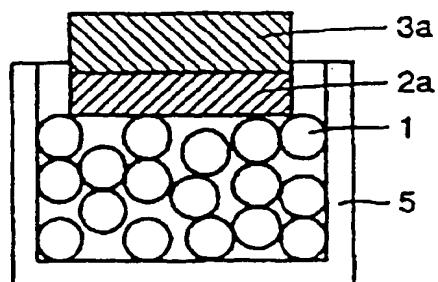


Fig.10

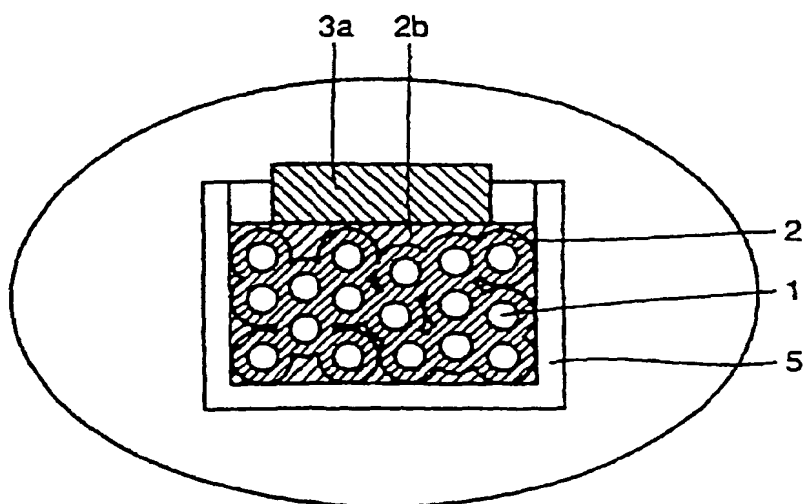


Fig.11

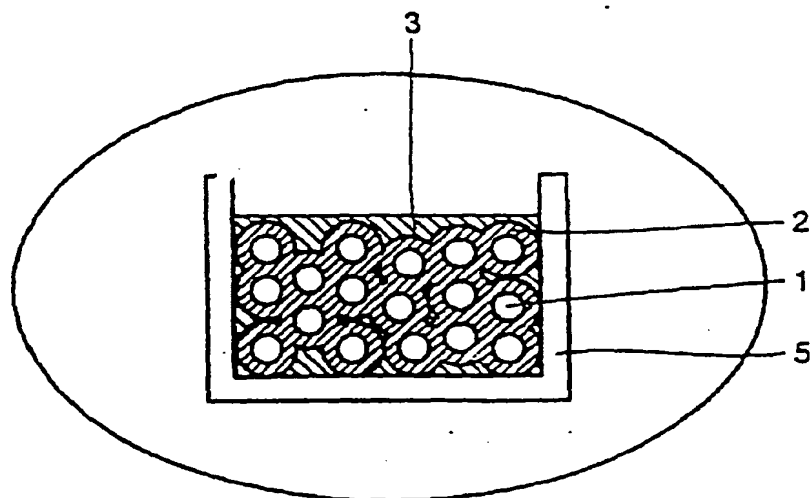


Fig.12

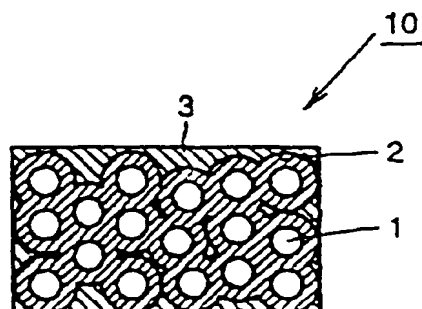


Fig.13(a)

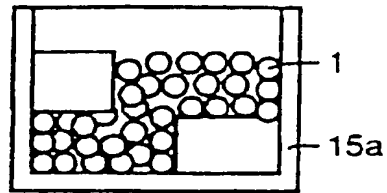


Fig.13(b)

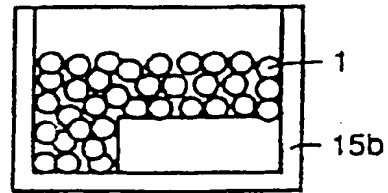


Fig.14(a)

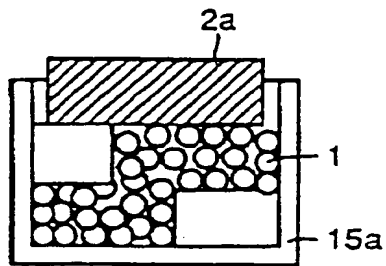


Fig.14(b)

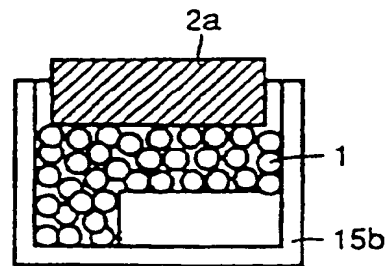


Fig.15(a)

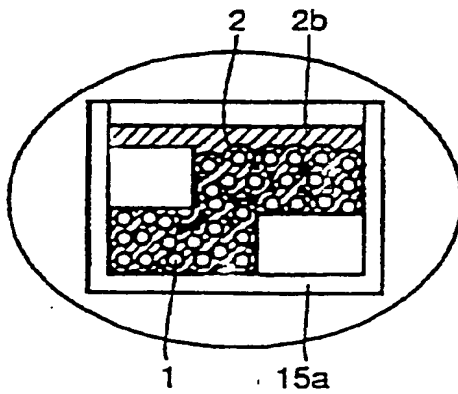


Fig.15(b)

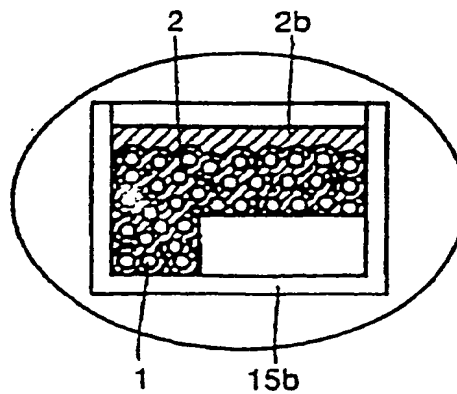


Fig.16(a)

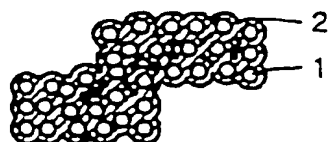


Fig.16(b)

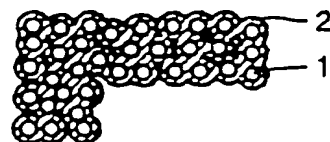


Fig.17(a)

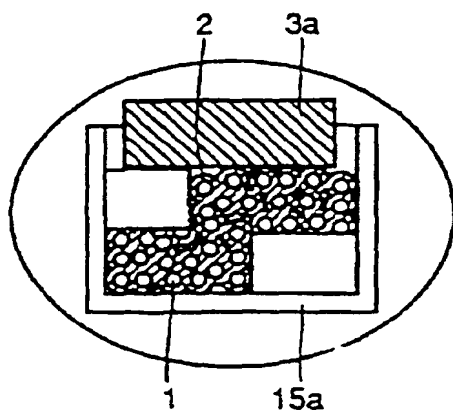


Fig.17(b)

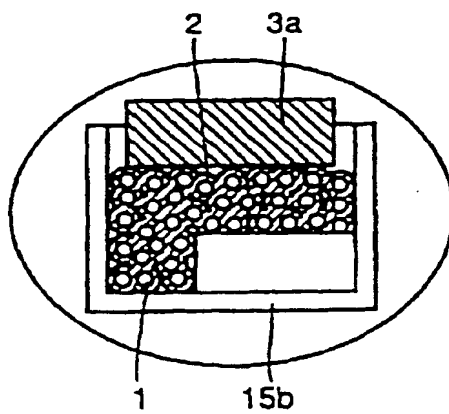


Fig.18(a)

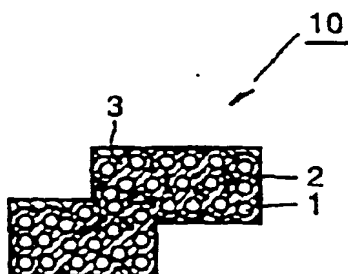


Fig.18(b)

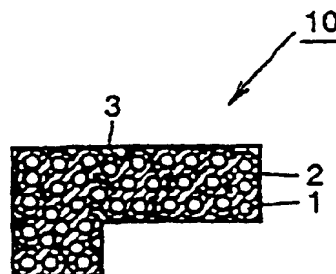
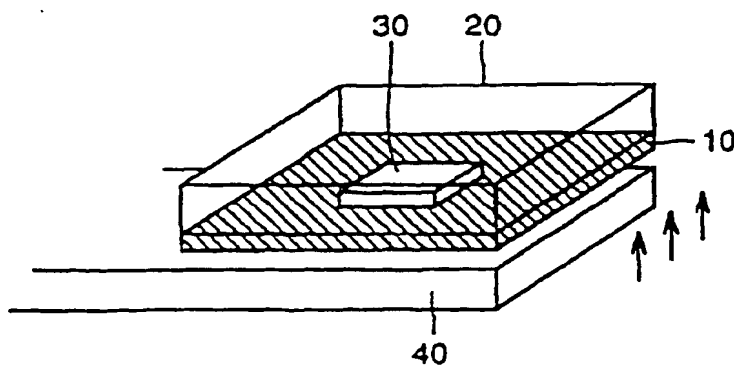
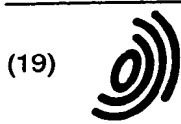


Fig.19





(19)

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(54) **Heat sink material for use with a semiconductor component and fabrication method thereof**

(57) A heat sink material for use with a semiconductor component having a coefficient of thermal expansion near to that of a semiconductor material and a high thermal conductivity, comprising a plurality of diamond particles, a metal, and a metal carbide, wherein the metal carbide and diamond particles constitute the matrix, and the metal fills the interstices of the matrix is provided. Also disclosed are a method for fabricating the same and a semiconductor package using the same.

**EP 0 859 408 A3**



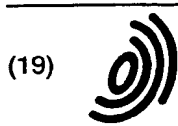
European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 98 10 2088

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                          |                                                  |                                              |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------|----------------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Citation of document with indication, where appropriate, of relevant passages                                                                                                                                            | Relevant to claim                                | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | KERNS J A ET AL: "DYMALLOY: A COMPOSITE SUBSTRATE FOR HIGH POWER DENSITY ELECTRONIC COMPONENTS" INTERNATIONAL JOURNAL OF MICROCIRCUITS AND ELECTRONIC PACKAGING, vol. 19, no. 3, 1 July 1996, pages 206-211, XP000639483 | 1,2,4,5,7,14                                     | H01L23/373                                   |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | "3. Fabrication of Dymalloy"<br>* page 208 *                                                                                                                                                                             | 3                                                |                                              |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | PATENT ABSTRACTS OF JAPAN vol. 095, no. 002, 31 March 1995 & JP 06 326432 A (DENKI KAGAKU KOGYO KK), 25 November 1994, * abstract *                                                                                      | 3                                                |                                              |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | EP 0 717 125 A (GEN ELECTRIC) 19 June 1996 * column 4, line 37 - column 5, line 12 *                                                                                                                                     | 8                                                |                                              |
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|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                          |                                                  | H01L                                         |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                          |                                                  |                                              |
| Place of search<br>MUNICH                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                          | Date of completion of the search<br>20 July 1998 | Examiner<br>Edmeades, M                      |
| CATEGORY OF CITED DOCUMENTS<br>X: particularly relevant if taken alone<br>Y: particularly relevant if combined with another document of the same category<br>A: technological background<br>O: non-written disclosure<br>P: intermediate document<br>T: theory or principle underlying the invention<br>E: earlier patent document, but published on, or after the filing date<br>D: document cited in the application<br>L: document cited for other reasons<br>&: member of the same patent family, corresponding document |                                                                                                                                                                                                                          |                                                  |                                              |

EPO FORM 1503 03.92 (P04C01)



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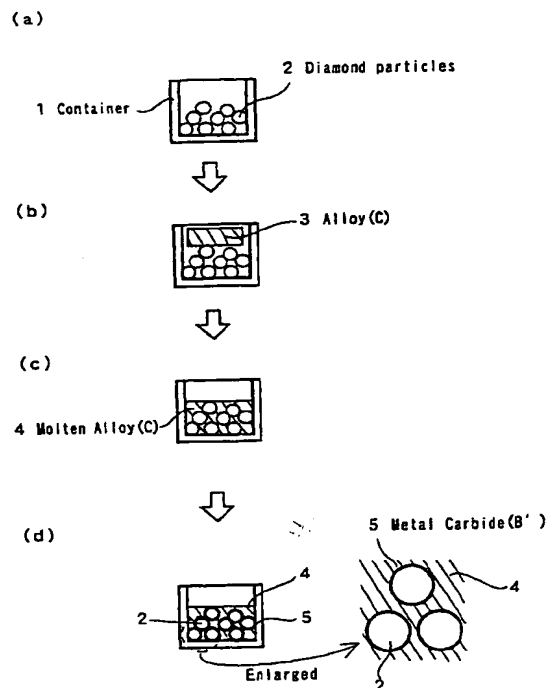
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(54) **Heat sink for semiconductors and manufacturing process thereof**

(57) A highly heat conductive heat sink comprising diamond particles yet eliminating heat distortion problems caused by the difference in thermal expansion with a semiconductor, and a manufacturing method thereof. Melting of an alloy (C), which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; and a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium, around diamond particles forms on the surface thereof a metal carbide (B'), which enables the strong bonding between the diamond particles and the metal (A) and thus produces a highly heat conductive heat sink having a much higher thermal conductivity than the metal (A). This structure is attainable by either an infiltration method or sintering method. A special feature, or effectiveness, of the invention lies in that the metal carbide (B') is formed on the surface of the diamond particles at the same time as or after the formation of a metal matrix. It is essential that not less than a quarter of the surface of the diamond particles be covered with the metal carbide (B') and the diamond particles be separated with one another by metal.

Fig. 1



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## Description

## BACKGROUND OF THE INVENTION

## 5 Field of the Invention

[0001] The present invention relates to a heat sink for heat dissipation of devices such as semiconductors and the manufacturing process thereof.

## 10 Description of the Background Art

[0002] Heat sinks are generally used as a means to cool semiconductors and other similar devices. Such heat sinks must instantaneously dissipate the heat that is rapidly produced in an element of semiconductors and other similar devices. To meet this requirement it is effective to use materials having a high heat dissipation property, which depends on the thermal conductivity and a specific heat thereof. Copper was once considered an appropriate candidate material because of its relatively high thermal conductivity of 398 W/mK and high specific gravity. However, copper has a coefficient of thermal expansion as high as 17 ppm/°C compared with that of semiconductors and ceramics for insulation; for example, 4.2 ppm/°C for silicon and 6.7 ppm/°C for GaAs. Consequently, when copper is joined with a semiconductor, due to the discrepancy in thermal expansion in the two components when the joined body is subjected to temperature variations both at the time of joining and during operation, too large a thermal stress is applied to the semiconductor, making this combination impractical in many instances.

[0003] Another idea is to use an alloy of copper and a metal having a small coefficient of thermal expansion such as tungsten or molybdenum. An alloy or dispersed body such as Cu-W or Cu-Mo system is used because the coefficient of thermal expansion of these materials is similar to that of a semiconductor. However, tungsten and molybdenum have a low thermal conductivity so that their alloys with copper exhibit conductivity no more than about 200 W/mK, which is less than desirable.

[0004] Another idea is to use a combination of metal and diamond, which has a high thermal conductivity. A variety of techniques stemming from this idea is disclosed in U.S. Pat. Nos. 5,045,972 and 5,130,771 and unexamined published Japanese patent applications Tokukaihei 3-9552 and Tokukaihei 4-231436. All these techniques take advantage of the high thermal conductivity of diamond in that by embedding it into metal and adjusting its volume ratio to bring the coefficient of thermal expansion of the total system closer to that of a semiconductor so that a thermal distortion caused by the difference in expansion between the two components will be eliminated when the joined body is subjected to temperature variations.

[0005] However, when diamond particles are simply embedded into a metal such as Cu, Ag, Au, and Al, due to poor bonding of diamond with these metals, the mechanical strength as a heat sink is intolerably weak and mixing cannot be performed thoroughly during the manufacturing process. To solve these problems, there is another idea, in which the surface of the diamond particles is coated with metal by special means before sintering with a metal such as Cu, Ag, Au, and Al. Although this method provides easy forming and enables the controlling of the composition, the final product manufactured with a conventional metal sintering process through mixing of powder, compacting under pressure, and sintering shows a thermal conductivity of no more than that of the metal used. In yet another method to cope with this problem, before embedding in a molten metal, diamond particles are coated with a metal capable of forming carbide with diamond. This method, although apparently similar to the invention, is not considered a solution to the problem because the metal used to produce the carbide remains around the diamond particles so that the excellent thermal conductivity of diamond cannot be fully utilized.

## 45 SUMMARY OF THE INVENTION

[0006] According to the invention to solve the aforementioned problem, a heat sink for semiconductor has a structure which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of the diamond particles, the heat sink having a structure wherein more than a quarter of the surface of individual diamond particles is covered with the metal carbide (B') and the diamond particles covered with the metal carbide (B') are separated from one another by the metal (A).

[0007] Such a structure provides increased bonding between the diamond particle and the surrounding metal, and also provides reasonable bonding between the diamond particle and the metal carbide (B') and around the same bonding between the metal carbide (B') and the neighboring metal (A). In thermal behavior, this structure can provide high thermal conductivity that is unattainable only with the metal (A). Especially, the condition wherein a quarter or more of the surface of the diamond particle is covered with the metal carbide (B') secures the strong bonding between the dia-

mond particle and the metal (A). When less than a quarter of the surface is covered, the bonding strength between the diamond particle and the metal (A) is insufficient, because at 150°C the heat sink softens and deforms by a load of 30 g/cm<sup>2</sup>. It is noted that the thinner layer of the metal carbide (B'), the better, because a trace of metal carbide that sticks to the surface of the diamond particle is sufficiently effective and a thicker layer has an adverse effect owing to the inferior thermal conductivity of the metal (B'). Another factor to reduce the thermal conductivity of a heat sink is the ample presence of the unreacted metal (B) around the diamond particles.

[0008] A metal (D) of at least one metal selected from the group consisting of tungsten, molybdenum, and alloys thereof may be dispersed in the metal (A). The metal (D) has a function of absorbing the difference in thermal expansion between the metal (A) and the diamond particles. It is preferable that the average diameter of the diamond particles be in a range of 60 to 700  $\mu\text{m}$ . If it is less than 60  $\mu\text{m}$ , the high thermal conductivity of the diamond cannot be exploited, and if more than 700  $\mu\text{m}$ , there is no room for the diamond particles to align in layer with thin heat sinks. It is further preferable that the ratio of the number of atoms in the metal (B) to that in the total heat sink be not less than 0.01 atm% and not more than 2.5 atm%. The metal (B) exists in the form of the metal carbide (B') around the individual diamond particles. When the metal carbide (B') covers less than a quarter of the diamond surface, which corresponds to less than 0.01 atm% in the ratio of the number of atoms, a strong bonding cannot be expected. Conversely, when the layer is too thick, corresponding to more than 2.5 atm%, a high thermal conductivity cannot be expected due to the inferior thermal conductivity of the metal carbide (B').

[0009] A more preferable solution is obtained when the metal (B) comprises at least one metal selected from the group consisting of Ti, Zr, and Hf, and the ratio of the number of atoms in the metal (B) to that in the total heat sink is not less than 0.01 atm% and not more than 2.5 atm%, because under these conditions a strong bonding is provided between the metal (B'), the diamond particles, and the metal (A) acting as a matrix, and a suitable thickness of the metal (B') is maintained so that the superior thermal conductivity of the diamond is utilized.

[0010] A yet more preferable result can be obtained when a metal (A) comprises an alloy of silver and copper under the condition that  $\text{Ag} \geq 0.6$  or  $\text{Cu} \geq 0.8$  in the volume ratio between the two is fulfilled. That the alloy is of silver and copper automatically signifies effectiveness in thermal conductivity, and it is essential to maintain the condition that either one of the component metals keeps its dominance over the other in the volume ratio. The reason is that given the greater ratio of either silver or copper, there are rich parts of either silver or copper in the alloy so that the total thermal conductivity becomes closer to that of the single metal itself.

[0011] Conversely, if the condition is either  $0.2 < \text{Ag} < 0.6$  or  $0.4 < \text{Cu} < 0.8$ , the thermal conductivity of the alloy parts dominates the total characteristic, failing to exhibit such a high thermal conductivity as the single metal itself does; i.e., the advantageous properties of diamond particles and metal cannot be exploited and the heat sink will suffer an inferior thermal conductivity.

[0012] A manufacturing method to form a heat sink comprising the metal (A), the metal carbide (B'), and the diamond particles may include the following:

- (a) putting a plurality of diamond particles in a container or mold;
- (b) putting an alloy (C) comprising the metal (A) and metal (B) in a container or mold together with the diamond particles at the same time or after the diamond particles are introduced; and
- (c) melting the alloy (C) with heat in a vacuum or at a pressure below 1000 atms so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') on the surface of individual diamond particles and the molten alloy (C) infiltrates into the gaps between the diamond particles.

[0013] Another manufacturing method for the same purpose may include the following:

- (a) putting a plurality of diamond particles in a container or mold;
- (b) putting the alloy (C) comprising the metal (A) and the metal (B) in a container or mold together with the diamond particles at the same time or after the diamond particles are introduced;
- (c) melting the alloy (C) with heat in a vacuum or at a pressure below 1000 atms so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') on the surface of individual diamond particles;
- (d) evaporating a part of the alloy (C) in a vacuum; and
- (e) infiltrating the metal (A), which is separately provided, in a vacuum or at a pressure below 1000 atms.

[0014] Yet another manufacturing method for the same purpose may include the following:

- (a) putting a plurality of diamond particles in a container or mold;
- (b) putting the alloy (C) comprising the metal (A) and the metal (B) together with the metal (A), which is separately provided, having a higher melting point than the alloy (C) in the container or mold together with the diamond parti-

cles at the same time or after the diamond particles are put;

(c) melting the alloy (C) with heat in a vacuum or at a pressure below 1000 atms so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') on the surface of individual diamond particles; and

(d) melting the separately provided alloy (A).

**[0015]** Contrary to the above, using the separately provided metal (A) having a lower melting point than the alloy (C) can achieve the same purpose. That is to say, the process may include the following:

(a) putting a plurality of diamond particles in a container or mold;

(b) putting the alloy (C) comprising the metal (A) and metal (B) together with the metal (A), which is separately provided, having a lower melting point than the alloy (C) in the container or mold together with the diamond particles at the same time or after the diamond particles are put;

(c) melting the separately provided metal (A) with heat in a vacuum or at a pressure below 1000 atms; and

(d) melting the alloy (C) so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') on the surface of individual diamond particles.

**[0016]** The above is a means called an infiltration method to manufacture the heat sink of the invention. The heat sink of the invention may also be manufactured by another means called a sintering method including the following:

(a) mixing powders of the alloy (C) comprising the metal (A) and the metal (B) with a plurality of diamond particles;

(b) pressure forming the mixture; and

(c) sintering the formed body at a temperature above the melting point of the alloy (C) so that the metal (B) included in the alloy (C) reacts with the diamond particles to form the metal carbide (B') around the diamond particles.

**[0017]** With the aforementioned method, an alternate method featuring the use of the separately provided metal (A) at the time of mixing to manufacture the heat sink of the invention may include the following:

(a) mixing powders of the alloy (C) comprising the metal (A) and the metal (B); powders of the metal (A), which are separately provided, having a higher melting point than the alloy (C); and a plurality of diamond particles;

(b) pressure forming the mixture; and

(c) sintering the formed body at a temperature above the melting point of the alloy (C) and below the melting point of the separately provided metal (A) so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') around the diamond particles.

**[0018]** Yet another sintering method to manufacture the heat sink of the present invention may include the following:

(a) mixing powders of the alloy (C) comprising the metal (A) and the metal (B); powders of the metal (D), which comprises at least one metal selected from the group consisting of tungsten, molybdenum, and alloys thereof, having a higher melting point than the alloy (C); and a plurality of diamond particles;

(b) pressure forming the mixture; and

(c) sintering the formed body at a temperature above the melting point of the alloy (C) and below the melting point of the metal (D) so that the metal (B) included in the alloy (C) reacts with the diamond particles to form the metal carbide (B') around the diamond particles.

**[0019]** This is a good method because it enables the adjustment of the coefficient of thermal expansion especially by the inclusion of at least one kind of the metal selected from the group consisting of tungsten, molybdenum, and alloys thereof.

**[0020]** Yet a further sintering method to manufacture the heat sink of the invention may include the following:

(a) mixing powders of the alloy (C) comprising the metal (A) and the metal (B); powders of the metal (A), which are separately provided, having a higher melting point than the alloy (C); and a plurality of diamond particles;

(b) pressure forming the mixture; and

(c) sintering the formed body at a temperature above the melting point of the separately provided metal (A) so that the metal (B) included in the alloy (C) reacts with the diamond particles to form the metal carbide (B') around the diamond particles.

**[0021]** The feature offered by the infiltration method is that the metal (A) and metal (B) constitute the alloy (C), which

is melted with heat in a vacuum or at a pressure below 1000 atms in contact with the diamond particles to enable the metal (B) released from the alloy (C) to disperse over the surface of individual diamond particles and form the metal carbide (B') as a result of the reaction with the diamond there. Because the metal (B) is more inclined to be carbonized when in contact with diamond than the metal (A), the metal carbide (B') is selectively produced, which encloses the diamond particles. Such processes are included in all of the above-mentioned four methods, any one of which, therefore, can supply the product of equivalent quality.

[0022] The feature offered by the sintering method as an alternative means is similar to that by the above-mentioned infiltration method in that when the diamond particles and powders of the alloy (C) are sintered inside the formed body, the metal (B) included in the alloy (C) reacts with the diamond particles to form the metal carbide (B') on the surface of the individual diamond particles. It is an important point in the invention that the metal (B) included in the alloy (C) reacts selectively with the diamond particles even when the formed body includes the metal (A) or metal (D). This point is common to the above-mentioned four methods.

[0023] According to the present invention, it is possible to furnish a heat sink with a high thermal conductivity, substantially higher than the thermal conductivity of the metal used, due to the superior thermal conductivity of diamond particles. Because the heat sink has an intermediate coefficient of thermal expansion between that of a heat sink with a metal base and that of diamond, thermal distortion problems caused by a joined semiconductor is effectively eliminated. Therefore, the present invention is especially effective in a heat sink for semiconductors that generate a large amount of heat or that generate heat instantaneously.

## BRIEF DESCRIPTION OF THE DRAWING

### [0024]

Fig. 1 is an illustration of a manufacturing method using the infiltration method of the invention. In steps (a) and (b), diamond particles 2 are put in a container 1 simultaneously with the alloy (C) 3 or before the alloy (C) 3 is introduced, and in step (c), the alloy (C) 3 is melted, the molten alloy (C) being 4. In step (d), the metal carbide (B') 5 is formed on the surface of individual diamond particles 2. The formed body is removed after it is cooled.

Fig. 2 illustrates another manufacturing method using the infiltration method of the invention. In steps (a) and (b), diamond particles 2 and the alloy (C) 3 are put in a container 1, and in step (c), the alloy (C) 3 is melted, the molten alloy (C) being 4. In step (d), the metal carbide (B') 5 is formed on the surface of individual diamond particles 2, and in step (e), a part of the molten alloy (C) 4 is evaporated. In step (f), the separately provided metal (A) 6 is added to infiltrate. The formed body is removed after it is cooled.

Fig. 3 shows yet another manufacturing method using the infiltration method of the invention. In steps (a) and (b), diamond particles 2 and the alloy (C) and the separately provided metal (A) 7 are put in a container 1. In step (c), the alloy (C) is melted, while the separately provided metal (A) is not melted yet, the two components being 8. In step (d), the metal carbide (B') 5 is formed, and in step (e), the separately provided metal (A) is melted; the molten alloy (C) and molten separately provided metal (A) together being 9. The formed body is removed after it is cooled.

Fig. 4 shows a manufacturing method using the sintering method of the invention. In step (a), diamond particles, powders of the alloy (C), and powders of the separately provided metal (A) are provided as the material, and in step (b), they are mixed. In step (c), the mixed materials are put in a mold to be subjected to pressure formation. The formed body is removed, and, in step (d), sintered in a furnace. In this process, the metal carbide (B') is formed on the surface of individual diamond particles. The sintered body is removed after it is cooled.

Fig. 5 is a graph showing the effects of the amount of the metal (B) in the invention.

Fig. 6 is a graph showing the ratio of composition when an alloy of silver and copper is used as the metal (A) in the invention and to show how the thermal conductivity of the heat sink is affected by the ratio.

Fig. 7 is a graph showing how the thermal conductivity of a heat sink is affected by the diameter.

## DETAILED DESCRIPTION OF THE INVENTION

[0025] The gist of the present invention is that a metal (B), which comprises at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium, forms a metal carbide (B') on the surface of individual diamond particles, and the metal carbide (B') is enclosed by a metal (A) comprising at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn, and the metal (A) constitutes the matrix of a heat sink. A heat sink formed only with diamond particles is ideal in terms of thermal conduction, but its thermal expansion is smaller than that of semiconductors and thus causes thermal distortions. This requires the absorption of the difference in thermal expansion between the two components by the metal (A). However, it is difficult to obtain sufficient bonding strength between the diamond particles and the metal (A). The present invention is to cope with this problem.

[0026] It is possible to maintain strong bonding between the diamond particles and the metal (A) by the intervention

of the metal carbide (B') made of the metal (B). The thermal conductivity can be improved by adding the superior conductivity of diamond to the conductivity of the single metal (A) itself. In addition, dispersion of the metal (D), which comprises at least one metal selected from the group consisting of tungsten, molybdenum, and alloys thereof, into the metal (A) creates an effect to absorb the difference in the coefficient of thermal expansion between the diamond particles and the metal (A) so that the more stable heat sink is obtained.

[0027] Thermal conduction is carried out by mutual transfer of heat between different kinds of material through the strongly bonded interface as in the present invention. If the bonding at the interface is insufficient, the thermal conduction is determined by the thermal conductivity specific to the material used as a matrix. More specifically, regardless of the amount of diamond particles having a high thermal conductivity that are embedded into the matrix of the metal (A), the thermal conduction as a whole is determined by the thermal conductivity of the metal (A) unless the bonding at the interface is of sufficient strength, offering little effect despite using expansive diamond particles.

[0028] When materials with different coefficient of thermal expansion are joined, thermal expansion causes an internal stress on either of the materials. The metal (A) is subjected to this stress in the present invention. The metal (A) around diamond particles has a larger coefficient of thermal expansion than diamond particles, whose coefficient of thermal expansion is as small as 1.5 ppm/°C in a range from room temperature to 200 °C. Hence, at an elevated temperature, the metal (A) is subjected to an internal stress due to the restriction by the smaller expansion of the diamond particles making the coefficient of thermal expansion of the heat sink as a whole smaller than that of the metal (A). To produce such condition evenly throughout the heat sink, it is desirable that the individual diamond particles be separately placed in the matrix of metal (A) without touching one another. Such a constitution enables the uniform distribution of the individual internal stress in the heat sink as a whole, thus preventing the distortion of the heat sink. The special feature of the present invention is that the heat sink has such a constitution as the diamond particles are covered with the metal carbide (B'), which, in turn, is enclosed by the metal (A).

[0029] In terms of bonding strength between the diamond and the metal (A), the best condition is that the metal carbide (B') encloses the entire surface of the diamond particles. However, it has been found that when at least a quarter of the surface of diamond particles is covered by the metal carbide (B'), a sufficient effect is obtained. To secure stable conditions, it is preferable that not less than half the surface of the diamond particles is covered with the metal carbide (B'). The remaining parts can be either the metal (A) or pores, though it is preferable to have fewer pores.

[0030] The choice of the diameter of the diamond particles depends on the size of the heat sink. If the particles are too small, the total thermal conductivity is reduced due to increased interfaces between the particles and the metal. If too large, it will limit the thickness of the heat sink. The reasonable diameter is between 60 and 700  $\mu\text{m}$ . The most preferable diameter is between 200 and 300  $\mu\text{m}$ .

[0031] The desirable volume ratio of the diamond particles to the total volume of the heat sink is 30 to 70 vol% taking into account thermal conductivity and expansion. If it is less than 30 vol%, an effective thermal conduction cannot be obtained. If more than 70 vol%, the adjustment of the coefficient of thermal expansion with a semiconductor becomes difficult, though the thermal conductivity will increase. When the volume ratio of the diamond particles lies between 45 and 65 vol%, the thermal conductivity is sufficiently high and the internal stress due to thermal expansion is suppressed, hence preferable.

[0032] The purpose of the metal carbide (B') is to improve the bonding strength between the diamond particles and the metal (A). If the volume of the metal carbide (B') is too large, the total thermal conductivity will decrease because of its poor thermal conductivity. If too small, the bonding strength cannot be improved. The desirable amount of the metal carbide (B') is between 0.01 and 2.5 atm% in the ratio of the number of atoms to that of the total heat sink. In this range, the bonding strength between the diamond particles and the metal (A) is sufficient, and the total thermal conductivity becomes larger than that of the metal (A) without suffering the reduction due to the presence of the metal carbide (B').

[0033] An especially preferable result will be given when the metal carbide (B') is formed by the metal (B) comprising at least one metal selected from the group consisting of Ti, Zr, and Hf and having a ratio of the number of atoms from 0.01 to 2.5 atm% of the total heat sink, because the effect of the metal carbide (B') becomes more evident. If the ratio of the number of atoms is less than 0.01 atm%, the amount will be insufficient to cover the surface of the diamond particles, so that the resultant bonding is too weak to prevent the deformation of the completed heat sink at an elevated temperature. If more than 2.5 atm%, the thermal conductivity will decrease due to the excessive amount of metal carbides against the total heat sink.

[0034] Furthermore, the metal (A) exhibits its utmost effect when it is composed of silver and copper. The volume ratio of silver or copper to the alloy determines the effect. More specifically, when  $\text{Ag} \geq 0.6$  if Ag is dominant and  $\text{Cu} \geq 0.8$  if Cu is dominant, the thermal conductivity becomes sufficiently high. Therefore, in the design of the composition of the metal (A), when a much larger volume ratio is allocated to either one of the constituents than the other, the total thermal conductivity approaches the conductivity of the dominant element, and a structure is obtained in which the superior thermal conductivity of diamond is readily exploited. The desirable volume ratio of an alloy differs with the selected element. The combination of silver and copper is the most desirable and the above-mentioned volume ratio is the most suitable to this combination. In this ratio, the use of titanium as the metal (B) exhibits a distinct effect. The data obtained from this com-

bination is shown in Fig. 6. Fig. 6 is a graph of the ternary system denoting the volume ratio of diamond particles, silver, and copper in a completed heat sink, indicating that the thermal conductivity of a completed heat sink varies with the volume ratio of silver and copper, both of which constitute the metal (A).

[0035] A heat sink with such a constitution can be manufactured by the processes described below. The first process is the infiltration method. Four methods in this category are described below. In the first method, a plurality of diamond particles are put in a container of a material having a higher melting point than the metal (A) and having little wettability to the metal (A), such as quartz or carbon, together with the alloy (C) made of the metal (A) and metal (B) at the same time or before the alloy (C) is added. The container is heated in a furnace in a vacuum or at a pressure below 1000 atms in a non-oxidizing atmosphere. In 0.5 to 10 minutes under these conditions, the metal (B) included in the alloy (C) is dispersed around the diamond particles to form the metal carbide (B') on the surface of the individual diamond particles, the alloy (C) itself infiltrating into the gaps between the diamond particles, reducing the total dimensions. The completed body is removed after it is cooled.

[0036] The second method is almost the same as the first except that the alloy (C) evaporates in a vacuum after melting. When the evaporation reaches a certain extent, a separately provided metal (A) is added and heated to infiltrate into the gaps in a vacuum or under a pressure below 1000 atms. The composition of the separately provided metal (A) may differ from that of the metal (A) included in the alloy (C).

[0037] The third method specifies the selection of the metal (A). Another metal (A) is separately provided apart from the metal (A) constituting the alloy (C) together with the metal (B). The separately provided metal (A) is so selected that it has a higher melting point than the alloy (C) so that the alloy (C) can selectively melt when it is heated together with the diamond particles and the separately provided metal (A) in a vacuum or at a pressure below 1000 atms.

[0038] When the alloy (C) is melted and the metal carbide (B') is formed on the surface of the diamond particles, there are two kinds of metal (A) in the container, i.e., the metal (A) included in the alloy (C) and the separately provided metal (A). Materials for the two kinds of metal (A) may either be the same or different from each other. When the same material is used, the metal (A) most decrease the melting point of the alloy (C) that the metal (A) constitutes with the metal (B). After the alloy (C) is melted, heating is continued to raise the temperature beyond the melting point of the separately provided metal (A) so that it can infiltrate into the gaps.

[0039] The fourth method also specifies the selection of the metal (A). Similarly, another metal (A) is separately provided in addition to the metal (A) constituting the alloy (C) together with the metal (B). The separately provided metal (A) is so selected that it has a lower melting point than the alloy (C) so that the separately provided metal (A) can selectively melt when it is heated together with the diamond particles and the alloy (C) in a vacuum or at a pressure below 1000 atms. When heated, the separately provided metal (A) will melt first and form liquid drops of molten metal between the diamond particles or at places remote from the diamond particles. Heating is continued to melt the alloy (C) so that it will infiltrate into the gaps between the diamond particles and the liquid drops of the metal (A), and the metal (B) released from the alloy (C) will react with the diamond particles to form the metal carbide (B'). Immediately after this reaction, the alloy (C) and the separately provided metal (A) are dispersed among the diamond particles. Under these conditions, a film of the metal carbide (B') is formed on the surface of the diamond particles, which is enclosed by the alloy (C), use gaps are filled by the separately provided metal (A). The above describes the manufacturing process by the infiltration method according to the present invention.

[0040] The other process to manufacture the heat sink according to the present invention is the sintering method. Four methods in this category are described below. In the sintering method all the materials except diamond particles are pulverized and mixed. By sintering the formed body, the metal (B) included in the alloy (C) is dispersed on the surface of the diamond particles to form the metal carbide (B').

[0041] In the first method, the diamond particles and powders of the alloy (C) made of the metal (A) and metal (B) are mixed. Although the mixing may be carried out by either a dry method or a wet method, the wet method by the use of an organic solvent or other agent is preferable to obtain a uniform mixture because the mixing is for different forms of materials such as particles and powders. The mixture, dried if necessary, is pressure formed in a mold. The formed body is sintered in a furnace. The sintering is performed in a non-oxidizing atmosphere or reducing atmosphere at a temperature slightly higher than the melting point of the alloy (C). When melting, the alloy (C) will enclose the diamond particles and the metal (B) included in the alloy (C) will react with the diamond particles at the surface to form the metal carbide (B'), producing the bonding between the diamond particles and the metal. Removed from the mold after cooling, the sintered body is ground and processed for finishing for the designed size of heat sink.

[0042] In the second method, the diamond particles are mixed with the powders of the alloy (C) made of the metal (A) and metal (B), and powders of the separately provided metal (A) having a higher melting point than the alloy (C). Although the mixing may be carried out by either the dry method or the wet method, the wet method by the use of an organic solvent or other agent is preferable to obtain a uniform mixture. The mixture is pressure formed in a mold. The formed body must be dried if wet mixing is employed. The formed body is sintered in a furnace. The sintering is performed at a temperature higher than the melting point of the alloy (C) and lower than that of the separately provided metal (A) to melt the alloy (C) selectively. The metal (B) included in the alloy (C) reacts with the diamond particles at the

surface to form the metal carbide (B'). The heating and cooling are carried out in a non-oxidizing atmosphere. If cooled without further heating, the separately provided metal (A) remains as powders. If the heating is continued, powders of the separately provided metal (A) melt to form a metal matrix together with the alloy (C). Either method can furnish the heat sink of the present invention.

[0043] In the third method, the same materials as the second method are provided. However, the formed body is sintered at a temperature higher than the melting point of the separately provided metal (A). Both the alloy (C) and the separately provided metal (A) melt at the same time and constitute a matrix. While melting, the metal (B) included in the alloy (C) forms the metal carbide (B') at the surface of the diamond particles. When a relatively large amount of diamond particles is used, the surface tension of the molten metal attracts diamond particles and keeps the form overcoming the contraction force. The probability that the metal (B) included in the alloy (C) contacts with the surface of the diamond particles and forms the metal carbide (B') is reduced due to the presence of the separately provided metal (A). When the metal carbide (B') is formed on at least a quarter of the surface of the diamond particles, the bonding between the diamond particles and metal is sufficient. The existence of pores in the completed product causes no problem.

[0044] The fourth method is a variation of the second method and the heat sink includes a metal (D) comprising at least one metal selected from the group consisting of tungsten, molybdenum, and alloys thereof. The diamond particles, powders of the alloy (C), and powders of the metal (D) are provided. Powders of a separately provided metal (A) may be added at the same time. The metal (D) has a higher melting point than the alloy (C) or the separately provided metal (A) because of the presence of tungsten and molybdenum. When a formed body made of the diamond particles, powders of the alloy (C), and powders of the metal (D)—and yet powders of the separately provided metal (A), if used—is heated in the sintering process, the metal (D) will not melt. The metal (D) has no influence on the metal (B) forming the metal carbide (B') on the surface of the diamond particles. Powders of the metal (D) are fixed on cooling by the alloy (C). Thus completed is a heat sink that includes the metal (D) in addition to the diamond particles, the metal carbide (B') over the same, and the metal (A). This heat sink makes it easy to adjust the coefficient of thermal expansion of the same with the help of the metal (D). Having an intermediate coefficient of heat expansion between the low coefficient of the diamond particles and the high coefficient of the metal (A), the metal (D) absorbs the stress concentration due to uneven thermal strain in the heat sink as a whole.

[0045] The methods described above are for the manufacture of the heat sink according to the present invention. Other methods may also be employed. As for the selection of materials for manufacture, the metal may be of either powder or mass in the infiltration method. In the sintering method, the metal should be of powder or granule. Especially, so that the powder of the alloy (C) adheres selectively to the surface of the diamond particles, the diamond particles and the pulverized alloy (C) should be mixed by a wet method with an organic solvent or other agent so that the diamond particles are enclosed by the alloy (C), before being mixed with other materials. In this way, the formation of the metal carbide (B') is secured.

[0046] Amounts of the diamond particles and the alloy (C) can be decided based on the designed figures of the thermal conductivity and coefficient of thermal expansion for the heat sink. It is essential to secure the amount of the metal (B) because the presence of the metal carbide (B') plays an important role in the property of the heat sink.

[0047] As mentioned above, there are at least eight methods to produce the heat sink according to the invention. All of them can produce a heat sink with a thermal conductivity better than that of the metals used and with a coefficient of thermal expansion smaller than that of the metal (A) and larger than that of diamond.

[0048] The heat sink according to the invention can be used alone, can be used in combination with other heat sinks, or can be used with surface plating. When the heat sink is joined with a semiconductor, it is desirable that solder of Au-Sn or Au-Ge alloy be used.

#### EXAMPLE 1

[0049] This example corresponds to the first method of infiltration. Diamond particles 200 to 300  $\mu\text{m}$  in diameter and the alloy (C) of the kind and volume ratio shown in Table 1 were put in a quartz container. The alloys (C) for the samples 1-1 to 1-8 were of a disk shape, and for the samples 1-9 to 1-12, of powder. The amount of the diamond particles was 55 to 65 % of the total volume of the heat sink. As for the alloy (C), the volume ratio between silver and copper included in the metal (A) is shown in Table 1; the kind and amount of the metal (B) are also shown in Table 1, where the amount is expressed in the ratio of the number of atoms to that of the total heat sink. The number of atoms of the metal is a value obtained by dividing the weight of the metal by its average atomic weight, for example. The reason for using this figure is that the effect of the metal (B) is determined not by the weight or volume but by the amount of atoms around the surface of the diamond particles.

[0050] For the samples 1-1 to 1-6, 1-9, and 1-10, the alloy (C) was melted at  $10^{-5}$  Torr or below in a vacuum chamber. For the samples 1-7 and 1-11, the alloy (C) was melted in a pressure vessel with an argon atmosphere at 1 atm; for the samples 1-8 and 1-12, at 3 atm. Kept for about 3 minutes after melting, the samples were removed after cooling to be finished for the designed size of the heat sink.

[0051] An outline of the process is shown in Fig. 1. The container used is of quartz, though carton containers may also be used. Even metal containers may be used if they hardly make a eutectic with the metal or alloy used as the material and they have a melting point higher than 1000°C. In this case, the metal container must be ground to remove the heat sink inside. Although the alloy (C) made of the metal (A) and the metal (B) is shown as a disk in Fig. 1, powders or granules can be used similarly. Powders may either be put on top of the mass of diamond particles or mixed with the diamond particles before being placed in the container.

[0052] Although the data is not shown, it was confirmed that even at a pressure higher than 10 atms the heat sink according to the invention can be produced by using a pressure-forming machine so long as an inert gas atmosphere is used.

[0053] The thermal conductivity of the completed heat sinks was measured by the laser flash method, and the results are shown in Table 1 along with those of the alloy (C). As can be seen in the table, the heat sink has a much higher thermal conductivity than the alloy (C). This proves that the metal (B) included in the molten alloy (C) reacted with the diamond particles and formed the metal carbide (B') on the surface of the diamond particles, furnishing the strong bonding between the diamond and metal. Analyses confirmed the existence of TiC, ZrC, and HfC on the surface of the diamond particles in the heat sink.

Table 1

| Sample No. | Contents of Alloy (C)    |                 |        | Melting Point (°C) | Thermal Conductivity |                        |
|------------|--------------------------|-----------------|--------|--------------------|----------------------|------------------------|
|            | Metal (A) (Volume Ratio) | Metal(B) (atm%) | Shape  |                    | Alloy(C) (W/mK)      | Heat Sink (n=5) (W/mK) |
| 1-1        | Ag:Cu=0.8:0.18           | Ti=0.3          | Disk   | 840                | 240                  | 470~520                |
| 1-2        | Ag:Cu=0.8:0.18           | Ti=0.6          | Disk   | 840                | 220                  | 430~480                |
| 1-3        | Ag:Cu=0.8:0.18           | Ti=1.2          | Disk   | 840                | 190                  | 390~440                |
| 1-4        | Ag:Cu=0.18:0.8           | Ti=0.6          | Disk   | 840                | 180                  | 400~450                |
| 1-5        | Ag:Cu=0.8:0.18           | Zr=0.6          | Disk   | 840                | 200                  | 430~490                |
| 1-6        | Ag:Cu=0.8:0.18           | Hf=0.6          | Disk   | 840                | 180                  | 400~450                |
| 1-7        | Ag:Cu=0.8:0.18           | Ti=0.3          | Disk   | 840                | 240                  | 460~520                |
| 1-8        | Ag:Cu=0.8:0.18           | Ti=0.3          | Disk   | 840                | 240                  | 470~520                |
| 1-9        | Ag:Cu=0.8:0.18           | Ti=0.3          | Powder | 840                | 240                  | 450~510                |
| 1-10       | Ag:Cu=0.8:0.18           | Ti=0.6          | Powder | 840                | 220                  | 420~470                |
| 1-11       | Ag:C=0.8:0.18            | Ti=0.3          | Powder | 840                | 240                  | 420~510                |
| 1-12       | Ag:Cu=0.8:0.18           | Ti=0.3          | Powder | 840                | 240                  | 440~490                |

Note: "n" means the number of samples.

## EXAMPLE 2

[0054] This example corresponds to the second method of infiltration. The same type of quartz container as used in example 1 was provided, wherein diamond particles 200 to 300 μm in diameter were added until they occupied 55 to 65 % of the total volume of the heat sink. The alloys (C) with various kinds and volumes were added as shown in Table 2 in the form of a disk for the samples 2-1 to 2-9 and in powder for the samples 2-10 and 2-11. The sample was heated in the same vacuum degree as example 1 to melt the alloy (C). It was kept under the same condition for 2 minutes, and then the sample was subjected to a temperature rise to evaporate the alloy (C) to such a degree that there exist gaps between the diamond particles. Observation of the removed sample showed that whereas the alloy (C) remained at the bottom of the container, at the upper part of the container there were gaps between the diamond particles with small amounts of the alloy (C) remaining. The sample in this state was put again into a vacuum chamber and the separately provided metal (A) shown in Table 2 was added with the same form and amount as the alloy (C) that was first added. Heating and vacuum treatment were resumed to melt the separately provided metal (A) so that the molten metal (A) can infiltrate into the gaps between the diamond particles. After the infiltration was assumed to be completed, the sample was cooled down to enable the removal of the formed heat sink from the container. Finishing process was per-

formed to obtain the designed heat sink. In example 2 also, although the results are not shown, it was possible to produce the desired heat sink with other alternatives in the processing condition such as a container material, an atmospheric condition, and a form of the alloy as described in example 1.

[0055] Thermal conductivity of the completed heat sinks is shown in Table 2. The results show that the heat sink has a higher thermal conductivity than the separately provided metal (A) or the alloy (C). This proves that the metal (B) has a great effect on the thermal conductivity of the completed heat sink.

[0056] An outline of the process in example 2 is shown in Fig. 2. Although the alloy (C) is shown as a disk in Fig. 2, powders of the same may be mixed with the diamond particles before inserting into the container.

Table 2

| Sample No. | Contents of Alloy (C)    |                  |        | Melting Point (°C) | Separately Provided Metal (A) | Thermal Conductivity   |
|------------|--------------------------|------------------|--------|--------------------|-------------------------------|------------------------|
|            | Metal (A) (Volume Ratio) | Metal (B) (atm%) | Shape  |                    | Kind and Volume Ratio         | Heat Sink (n=5) (W/mK) |
| 2-1        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 860                | Ag                            | 680~730                |
| 2-2        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 860                | Cu                            | 600~650                |
| 2-3        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 860                | Au                            | 510~560                |
| 2-4        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 860                | Al                            | 460~520                |
| 2-5        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 860                | Mg                            | 280~340                |
| 2-6        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 860                | Zn                            | 230~260                |
| 2-7        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 860                | Ag:Cu=0.8:0.2                 | 640~690                |
| 2-8        | Ag:Cu=0.8:0.16           | Ti=0.6           | Disk   | 860                | Ag:Cu=0.2:0.8                 | 620~670                |
| 2-9        | Ag:Cu=0.8:0.16           | Ti=1.2           | Disk   | 860                | Ag                            | 660~720                |
| 2-10       | Ag:Cu=0.8:0.18           | Ti=0.6           | Powder | 860                | Ag (Powder)                   | 680~740                |
| 2-11       | Ag:Cu=0.8:0.18           | Ti=0.6           | Powder | 860                | Cu (Powder)                   | 590~640                |

Note: "n" means the number of samples.

### EXAMPLE 3

[0057] This example corresponds to the third method of infiltration. The diamond particles having the same size and volume as described in example 1 were put into a quartz container. The alloys (C) and separately provided metal (A) were added, as shown in Table 3, each in a form of disk for the samples 3-1 to 3-8 and in a form of powder for the samples 3-9 and 3-10. When powder were used, they were mixed with the diamond particles before inserting into the container. The alloy (C) and the metal (A) are the same weight. The sample was heated under the same vacuum condition as example 1 to selectively melt the alloy (C). Because the alloy (C) has a lower melting point than the separately provided metal (A) to which it is combined, the alloy (C) melted first. The conditions were kept unchanged for 5 minutes to form the metal carbide (B'). Then the temperature was raised to melt the metal (A). Without the alloy (C), the metal (A) has no power to infiltrate into the gaps between the diamond particles because it has poor wettability to diamond. However, when the metal carbide (B') is formed on the surface of the diamond particles due to the melting of the alloy (C), the metal (A) starts its infiltration because it has good wettability to the alloy. The sample was cooled down to remove the formed heat sink from the container. The finishing process was performed to obtain the designed size of the heat sink. An outline of the manufacturing process for this example is shown in Fig. 3.

[0058] Thermal conductivity of the completed heat sinks is shown in Table 3. The results show that the heat sink produced in such a manner as described above has a higher thermal conductivity than the metal used.

Table 3

| Sample No. | Contents of Alloy (C)    |                  |        | Melting Point (°C) | Separately Provided Metal (A) | Thermal Conductivity   |
|------------|--------------------------|------------------|--------|--------------------|-------------------------------|------------------------|
|            | Metal (A) (Volume Ratio) | Metal (B) (atm%) | Shape  |                    | Kind and Volume Ratio         | Heat Sink (n=5) (W/mK) |
| 3-1        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 830                | Ag                            | 600~650                |
| 3-2        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 830                | Cu                            | 510~570                |
| 3-3        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 830                | Ag:Cu=0.9:0.1                 | 580~630                |
| 3-4        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk   | 830                | Ag:Cu=0.1:0.9                 | 560~610                |
| 3-5        | Ag:Cu=0.7:0.28           | Ti=0.6           | Disk   | 830                | Ag                            | 570~630                |
| 3-6        | Ag:Cu=0.7:0.28           | Ti=0.6           | Disk   | 830                | Cu                            | 500~550                |
| 3-7        | Ag:Cu=0.8:0.18           | Ti=0.3           | Disk   | 830                | Ag                            | 630~680                |
| 3-8        | Ag:Cu=0.8:0.16           | Ti=1.2           | Disk   | 830                | Ag                            | 580~630                |
| 3-9        | Ag:Cu=0.8:0.18           | Ti=0.6           | Powder | 830                | Ag (Powder)                   | 580~640                |
| 3-10       | Ag:Cu=0.8:0.18           | Ti=0.6           | Powder | 830                | Cu (Powder)                   | 500~560                |

Note: "n" means the number of samples.

## EXAMPLE 4

[0059] This example corresponds to the fourth method of infiltration. Diamond particles 200 to 300  $\mu\text{m}$  in diameter, a disk of the alloy (C), and a disk of the separately provided metal (A) shown in Table 4 were put into a quartz container. The samples 4-1 to 4-5 are heated at  $10^{-5}$  Torr in a vacuum chamber. The samples 4-6 and 4-7 are heated in an argon gas atmosphere at 1 atm; the sample 4-8, at 3 atm in a pressure vessel. The heating temperature was raised and kept for a while at a temperature roughly equal to the melting point of the metal (A), and then raised to the melting point of the alloy (C). Before the melting of the alloy (C), the molten metal (A) was insufficiently distributed in a form of liquid drops between the diamond particles and on the surface area of the mass of the diamond because it has poor wettability to diamond. Once the alloy (C) was melted, the metal (B) included in the alloy (C) formed the metal carbide (B') on the surface of the diamond particles, and the molten metal (A) infiltrated into the gaps between the diamond particles because it has good wettability to the alloy.

[0060] Kept for 2 minutes after the temperature was raised to the melting point of the alloy (C), the sample was gradually cooled down. When it was cooled to room temperature, it was removed from the container to be finished for the designed size of the heat sink.

[0061] The amount of the diamond particles used in this example was 55 to 65 % of the total volume of the completed heat sink. The weight of the alloy (C) was the same as the metal (A). The amount of the metal (B) included in the alloy (C) was 0.6 atm% for all the samples shown in Table 4, where the amount is expressed in the ratio of the number of atoms to that of the total heat sink.

[0062] Measured results of the thermal conductivity of the completed heat sinks are shown in Table 4. These results confirmed that the heat sink has a higher thermal conductivity than the alloy or the metal used. It is noted that the samples 4-4 and 4-5 showed comparable data to those obtained with the samples having the same Ag-Cu system metal shown in examples 2 and 3. As for the heating environment, the results obtained with samples prepared in a vacuum, under atmospheric pressure, or under pressurized conditions showed no significant difference so long as an inert gas environment was used as is seen with the samples 4-1, 4-6, and 4-8.

Table 4

| Sample No. | Contents of Alloy (C)    |                  |       | Melting Point (°C) | Separately Provided Metal (A) | Thermal Conductivity   |
|------------|--------------------------|------------------|-------|--------------------|-------------------------------|------------------------|
|            | Metal (A) (Volume Ratio) | Metal (B) (atm%) | Shape |                    | Kind and Volume Ratio         | Heat Sink (n=5) (W/mK) |
| 4-1        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk  | 830                | Al                            | 330~380                |
| 4-2        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk  | 830                | Mg                            | 230~290                |
| 4-3        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk  | 830                | Zn                            | 180~240                |
| 4-4        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk  | 830                | Ag:Cu=0.8:0.2                 | 580~630                |
| 4-5        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk  | 830                | Ag:Cu=0.2:0.8                 | 560~610                |
| 4-6        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk  | 830                | Al                            | 350~400                |
| 4-7        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk  | 830                | Mg                            | 240~280                |
| 4-8        | Ag:Cu=0.8:0.18           | Ti=0.6           | Disk  | 830                | Al                            | 350~410                |

Note: "n" means the number of samples.

## EXAMPLE 5

[0063] This example corresponds to the second method of sintering. Diamond particles 200 to 300  $\mu\text{m}$  in diameter, powders of the alloy (C), and powders of the separately provided metal (A) shown in Table 5 were mixed. The amount of the diamond particles was 40 to 50 % of the total volume of the heat sink. As for the alloy (C), the volume ratio between silver and copper included in the metal (A) is shown in Table 5; the amount of the metal (B) is also shown in Table 5, where the amount is expressed in the ratio of the number of atoms to that of the total heat sink. The metal (A) was so selected that it has a higher melting point than the alloy (C). The weight of the alloy (C) was the same as that of the metal (A). For comparison purpose, the samples 5-3 and 5-6 were prepared as the samples without the alloy (C), and the sample 5-7, without the metal (A).

[0064] A mixed body of the diamond particles and powders was pressure formed to the designed form by a press at a pressure of about 2000  $\text{kg}/\text{cm}^2$ . The formed body was put into a sintering furnace and heated in an inert gas atmosphere to a temperature beyond the melting point of the alloy (C), with the temperature kept for 1 minute. Gradually cooled to the ambient temperature, the sample was ground to the designed size.

[0065] The measured results of the thermal conductivity of the completed heat sinks are shown in Table 5 along with those of the metal part only. The results show that the metal (B) included in the alloy (C) plays an important role in determining the total thermal conductivity of the completed heat sink, because the samples without the metal (B) showed a lower thermal conductivity than others as is seen in the data with the samples 5-3 and 5-6. Analyses confirmed the existence of TiC on the surface of the diamond particles in the heat sink so produced as described above; i.e., the formation of the metal carbide (B') was confirmed. The observation of the diamond particles appearing on the cross section when a completed heat sink was dissected at several points revealed that a film of TiC covers a quarter or more of the surface of the diamond particles, not necessarily the entire surface.

[0066] An outline of the process in example 5 is shown in Fig. 4. Diamond particles, powders of the alloy (C), and powders of the metal (A) were mixed by a mixer. The mixed body was pressure formed to the designed form by a press. The formed body was heated in an inert gas or reducing atmosphere in a vacuum, under atmospheric pressure, or under a pressurized condition to a temperature of sintering for the alloy (C), with the temperature kept for 1 minute. If no alloy (C) was used, the temperature condition was used for the single metal (A). Gradually cooled to the ambient temperature, the sintered body was ground to the designed size of the heat sink. As for the samples 5-3 and 5-6 having no alloy (C), grinding the same took time because of the poor bonding between the diamond particles and the metal (A) causing strong grinding to crumble the form.

Table 5

| Sample No. | Contents of Alloy (C)    |                  | Melting Point (°C) | Separately Provided Metal (A) | Thermal Conductivity |                        |
|------------|--------------------------|------------------|--------------------|-------------------------------|----------------------|------------------------|
|            | Metal (A) (Volume Ratio) | Metal (B) (atm%) |                    |                               | Metal Part (W/mK)    | Heat Sink (n=5) (W/mK) |
| 5-1        | Ag:Cu=0.78:0.2           | Ti=0.6           | 830                | Ag                            | 300                  | 570~620                |
| 5-2        | Ag:Cu=0.9:0.08           | Ti=0.6           | 830                | Ag                            | 390                  | 680~740                |
| 5-3        | None                     | None             | 830                | Ag                            | 400                  | 210~260                |
| 5-4        | Ag:Cu=0.78:0.2A          | Ti=0.6           | 830                | Cu                            | 100                  | 330~370                |
| 5-5        | g:Cu=0.08:0.9            | Ti=0.6           | 830                | Cu                            | 360                  | 580~630                |
| 5-6        | None                     | None             | 830                | Cu                            | 380                  | 180~240                |
| 5-7        | Ag:Cu=0.78:0.2           | Ti=0.6           | 830                | None                          | 250                  | 280~330                |

Note: "n" means the number of samples.

## EXAMPLE 6

[0067] This example was carried out to examining the effect of sintering temperature upon the thermal conductivity of the completed heat sink. The same combination of diamond particles, powders of the alloy (C), and powders of the separately provided metal (A) as used in the sample 5-1 in example 5 was used. Samples were kept at a sintering temperature between 600 and 900 °C for 1 minute as in example 5. The measured results of the thermal conductivity of the completed heat sinks are shown in Table 6. The data of the samples 6-1 and 6-2 show that the thermal conductivity of the completed heat sink is substantially lower than that of the metal part, manifesting no effect of the diamond. Observation of the surface of the diamond particles on a cross section when a completed heat sink was dissected revealed that no TiC was formed. The results confirmed that below the melting point of the alloy (C), 830 °C, the bonding between the diamond particles and the metal is insufficient and no effect of composition of materials is obtained.

Table 6

| Sample No. | Sintering Temperature (°C) | Thermal Conductivity |                        |
|------------|----------------------------|----------------------|------------------------|
|            |                            | Metal Part (W/mK)    | Heat Sink (n=5) (W/mK) |
| 6-1        | 600                        | 220                  | 30~70                  |
| 6-2        | 750                        | 250                  | 80~140                 |
| 6-3        | 830                        | 300                  | 620~680                |
| 6-4        | 850                        | 320                  | 570~610                |
| 6-5        | 900                        | 310                  | 540~600                |

Note: "n" means the number of samples.

## EXAMPLE 7

[0068] This example was carried out to clarify the effect of the metal (B) upon the thermal conductivity of the completed heat sink. A mixed body of the diamond particles, having about a 300 µm diameter and occupying 40 to 50 % of the total volume of the heat sink, and powders of the alloy (C) shown in Table 7 was pressure formed at about 2000 kg/cm<sup>2</sup>. The formed bodies of the samples 7-1 to 7-7 were put in a sintering furnace and sintered in a hydrogen gas atmosphere at 1 atm. The samples 7-8 and 7-9 were put in a vacuum chamber and sintered in a vacuum of 10<sup>-5</sup> Torr or below. Kept for 0.5 minutes under the sintering condition and cooled, the sample was then ground to the designed

size of heat sink. Thermal conductivity of the heat sinks is shown in Table 7. The samples 7-1 and 7-7 do not have the metal (B) to be included in the alloy (C). Because they only have the separately provided metal (A), sintering did not proceed and the samples disintegrated without achieving the desired formation. In contrast to this, the samples having the metal (B) included in the alloy (C) exhibit a much higher thermal conductivity than the metal used.

Table 7

| Sample No. | Contents of Alloy (C)    |                  | Melting Point (°C) | Thermal Conductivity   |
|------------|--------------------------|------------------|--------------------|------------------------|
|            | Metal (A) (Volume Ratio) | Metal (B) (atm%) |                    | Heat Sink (n=5) (W/mK) |
| 7-1        | Ag:Cu=0.78:0.2           | None             | 870                | Sample Not Formed      |
| 7-2        | Ag:Cu=0.88:0.1           | Ti=0.6           | 870                | 670~710                |
| 7-3        | Ag:Cu=0.83:0.15          | Ti=0.6           | 870                | 565~615                |
| 7-4        | Ag:Cu=0.78:0.2           | Ti=0.6           | 870                | 280~320                |
| 7-5        | Ag:Cu=0.2:0.78           | Ti=0.6           | 870                | 330~370                |
| 7-6        | Ag:Cu=0.1:0.88           | Ti=0.6           | 870                | 580~640                |
| 7-7        | Ag:Cu=0.2:0.78           | None             | 870                | Sample Not Formed      |
| 7-8        | Ag:Cu=0.88:0.1           | Ti=0.6           | 870                | 650~710                |
| 7-9        | Ag:Cu=0.83:0.15          | Ti=0.6           | 870                | 575~625                |

Note: "n" means the number of samples.

## EXAMPLE 8

[0069] This example was conducted to examine the effect of the ratio of the number of atoms in the metal (B) using the materials similar to those used in example 5. Diamond particles had diameters between 200 and 300  $\mu\text{m}$ . The separately provided metal (A) was a purified silver or copper. The alloy (C) comprises the metal (A) of the Ag-Cu system and the metal (B) of titanium. The resultant system is a quaternary system of diamond-Ag-Cu-Ti. To observe the effect of the metal (B), the ratio of the number of atoms of titanium to that of the total heat sink was varied from 0 to 8 atm%, whereas the amount of the diamond particles was fixed at about 50 vol% and two values of the volume ratio of silver were used; 90 % and 20%.

[0070] The diamond particles, powders of the alloy (C), and powders of the metal (A) were mixed by a ball mill to be formed at a pressure between 1000 and 7000  $\text{kg/cm}^2$ —mainly at 2000  $\text{kg/cm}^2$ . The formed body was sintered in a hydrogen atmosphere under atmospheric pressure. The sintered sample was ground to the designed size. The measured results of the thermal conductivity on the samples are shown in Fig. 5, wherein omitted are the data for more than 4 atm% in the ratio of the number of atoms of the metal (B), titanium in this case.

[0071] This result shows that the thermal conductivity of the heat sink exceeds that of silver when the ratio of the number of atoms of titanium to that of the total heat sink lies between 0.01 and 2.5 atm%, inclusive. Similar data is obtained when zirconium or hafnium is used as the metal (B). In summary, the above results demonstrate that the most suitable amount of the metal (B) lies between 0.01 and 2.5 atm%, inclusive.

## EXAMPLE 9

[0072] In selecting the metal (A) to be included in the alloy (C), it must be noted that some candidates are very effective while others are not. Especially for the Ag-Cu system, it is desirable that the ratio be so selected that either metal can exist as a single metal, because an alloy of silver and copper reduces the thermal conductivity of the constituent metals. This example was conducted to clarify the effect of the composition of the metal (A). The sample was prepared by the infiltration method described in example 1, with the Ag-Cu system as the metal (A) and titanium as the metal (B). Diamond particles, having diameters from 200 to 300  $\mu\text{m}$  and a volume varied from 40 to 65 % of the total heat sink, were put into a quartz container, and a disk of Ag-Cu-Ti alloy as the alloy (C) was placed there. The sample was heated in an argon gas atmosphere at 3 atm in a pressure vessel to infiltrate the alloy (C) into the gaps between the diamond particles. Kept for 3 minutes under the heating condition and the cooled to a room temperature, the sample was ground to the designed size of the heat sink. As the composition variation in the alloy (C) in manufacturing samples, the ratio between silver and copper was varied and the ratio of the number of atoms of titanium to that of the total heat sink was

varied from 0.5 to 1 atm%.

[0073] The measured results of thermal conductivity of the heat sinks are shown as a graph in Fig. 6. Fig. 6 is a ternary graph wherein each apex of the triangle shows the 100 % volume of the material written there. The graph shows the variation of the thermal conductivity of the heat sink due to the variation of the ratio between silver and copper, with the volume of diamond particles varied from 40 to 65 %. In this graph, the large circle shows that the thermal conductivity is more than 500 W/mK; the small circle, more than 400 W/mK; and the square, less than 300 W/mK. It is clear that the thermal conductivity of the heat sink is affected by the ratio between silver and copper. More specifically, when the value  $Ag/(Ag+Cu)$  is more than 0.6 or the value  $Cu/(Ag+Cu)$  is more than 0.8, the thermal conductivity exhibits a higher value. The reason for this tendency is considered to be that the existence of a single metal rather than an alloy maintains and improves the total thermal conductivity because the thermal conductivity of the alloy of silver and copper exhibits extremely low value compared with that of the constituent metals themselves. Therefore, when the Ag-Cu system is used as the metal (A), the present invention is most effectively embodied when the above-mentioned ratio is applied.

#### EXAMPLE 10

[0074] This example corresponds to the fourth method of sintering. In Fig. 4, powders of the separately provided metal (A) were replaced by powders of the metal (D). Diamond particles having an average diameter of about 300  $\mu m$  were used and the volume ratio thereof to the total heat sink was 40 to 50%. The volume ratio of the metal (A) in the alloy (C) and the ratio of the number of atoms of the metal (B) are shown in Table 8. In accordance with the process shown in Fig. 4, diamond particles and metal powders were mixed and pressed at 2000 kg/cm<sup>2</sup>. The formed body was sintered in a hydrogen reducing atmosphere under atmospheric pressure at a temperature beyond the melting point of the alloy (C) in a sintering furnace. After cooling the sintered body was ground to the designed size of the heat sink.

[0075] Thermal conductivity of the completed heat sinks is shown in Table 8 along with those of metal parts alone. The data obtained with the samples 5-1 and 5-5, having the metal (A) instead of the metal (D), in example 5 are cited in Table 8 as a reference. The results show that the thermal conductivity of the completed heat sinks is much higher than that of the metal parts alone. It was observed that powders of tungsten or molybdenum in the heat sink were distributed among the diamond particles without congregating, so that heat is conducted principally through silver or copper parts in the alloy (C) without the intervention of the additional metal powder. The primal function of tungsten and molybdenum is to absorb the thermal stress in the heat sink by their intermediate amount of expansion between the diamond and the metal (A) when heated.

Table 8

| Sample No. | Contents of Alloy (C)    |                  | Melting Point (°C) | Separately Provided Metal (A) or (D) (Kind) | Thermal Conductivity |                        |
|------------|--------------------------|------------------|--------------------|---------------------------------------------|----------------------|------------------------|
|            | Metal (A) (Volume Ratio) | Metal (B) (atm%) |                    |                                             | Metal Part (W/mK)    | Heat Sink (n=5) (W/mK) |
| 8-1        | Ag:Cu=0.78:0.2           | Ti=0.6           | 870                | W (D)                                       | 190                  | 380~420                |
| 8-2        | Ag:Cu=0.08:0.9           | Ti=0.6           | 870                | W (D)                                       | 180                  | 365~415                |
| 8-3        | Ag:Cu=0.78:0.2           | Ti=0.6           | 870                | Mo (D)                                      | 160                  | 340~380                |
| 8-4        | Ag:Cu=0.08:0.9           | Ti=0.6           | 870                | Mo (D)                                      | 150                  | 335~385                |
| 5-1        | Ag:Cu=0.78:0.2           | Ti=0.6           | 830                | Ag (A)                                      | 300                  | 570~620                |
| 5-5        | Ag:Cu=0.08:0.9           | Ti=0.6           | 830                | Ca (A)                                      | 360                  | 580~630                |

Note: "n" means the number of samples.

#### EXAMPLE 11

[0076] This example was performed to examine the effect of sintering temperature. Diamond particles having an average diameter of about 300  $\mu m$  and a volume ratio of 40 to 50% to the total heat sink, powders of the alloy (C), and powders of the separately provided metal (A) shown in Table 9 were mixed to be pressure formed. The formed body was

sintered in a hydrogen atmosphere at a temperature shown in Table 9 in a sintering furnace. The samples 9-3 and 9-6 having no alloy (C) disintegrated during the sintering process without achieving the desired formation. The sintering temperature used was the melting point of the separately provided metal (A) that melts at a higher temperature than the alloy (C). Table 9 shows that the completed heat sink has a much higher thermal conductivity than the metal used. The samples in Table 9 have the same composition as those in Table 5 for example 5; for instance, the sample 9-1 corresponds to 5-1. It is clear that the sample 9-1 has a noticeably higher thermal conductivity than the sample 5-1. This difference is attributable to the difference in the sintering temperature; the sample 9-1 was sintered at 980 °C, whereas the sample 5-1, at about 830 °C. Observation of sections of a completed heat sink of this example reveals that the sample has no different phases of two metal parts, the alloy (C) and the metal (A), which exist in the sample made by example 5. It is considered that this uniform metal phase is the reason why the samples in this example have a higher thermal conductivity than those in example 5.

Table 9

| Sample No. | Contents of Alloy (C)    |                  | Sintering Temp. (°C) | Separately Provided Metal (A) | Thermal Conductivity |                        |
|------------|--------------------------|------------------|----------------------|-------------------------------|----------------------|------------------------|
|            | Metal (A) (Volume Ratio) | Metal (B) (atm%) |                      |                               | Metal Part (W/mK)    | Heat Sink (n=5) (W/mK) |
| 9-1        | Ag:Cu=0.78:0.2           | Ti=0.6           | 980                  | Ag                            | 300                  | 690~730                |
| 9-2        | Ag:Cu=0.9:0.08           | Ti=0.6           | 980                  | Ag                            | 390                  | 750~810                |
| 9-3        | None                     | None             | 980                  | Ag                            | 400                  | Not Formed             |
| 9-4        | Ag:Cu=0.78:0.2           | Ti=0.6           | 1100                 | Cu                            | 100                  | 440~480                |
| 9-5        | Ag:Cu=0.08:0.9           | Ti=0.6           | 1100                 | Cu                            | 360                  | 660~720                |
| 9-6        | None                     | None             | 1100                 | Cu                            | 380                  | Not Formed             |

Note: "n" means the number of samples.

## EXAMPLE 12

[0077] This example was conducted to examine the effect of the diameter of the diamond particles upon the thermal conductivity of the heat sink. For this purpose, the average diameter of the diamond particles was varied with other conditions unchanged from those in the sample 5-1 in example 5. The volume ratio of the diamond particles was adjusted to 50 % of the total heat sink. Measured results are summarized in a graph in Fig. 7, where the axis of abscissa represents the average diameter of the diamond particles, and the axis of ordinate, the thermal conductivity of the completed heat sink. As is seen in the graph, the thermal conductivity decreases with the decreasing diameter. It is noted that when the diameter is not more than 60  $\mu\text{m}$ , the thermal conductivity becomes lower than that of the metal (A), silver in this case. The reason is that the reduction in diamond diameter brings the increase in the percentage of the metal carbide that exists in the heat path. The metal carbide (B') formed on the surface of the diamond particles has poor thermal conductivity and has a tendency to reduce the total thermal conductivity despite the high conductivity of the diamond. In this sense, the larger the diameter of the diamond particles, the better. However, if the diameter is too large, the diamond particles cannot compose a thin heat sink and the metal cannot absorb the thermal stress caused by the difference in expansion between the diamond particles and the metal. Nothing serious takes place when the diameter is less than 700  $\mu\text{m}$ , and beyond that cracks may appear at the time of bonding with a semiconductor substrate. In conclusion, it is desirable that the diameter of the diamond particles be between 60 and 700  $\mu\text{m}$ , inclusive, in the present invention.

## Claims

1. A heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of diamond particles, the heat sink having a structure wherein not less than a quarter of the surface of the individual diamond particles is covered with the metal carbide (B') and the diamond particles covered with the metal carbide (B') are separated with one another by the metal (A).

2. The heat sink as defined in claim 1, wherein a layer of the metal (B) is not formed around the metal carbide (B') which covers the diamond particles.
3. The heat sink as defined in claim 1 or 2, wherein the metal (A) further includes a metal (D) of at least one metal selected from the group consisting of tungsten, molybdenum, and alloys thereof.
4. The heat sink as defined in claim 1 or 2, wherein the average diameter of the diamond particles lies between 60 and 700  $\mu\text{m}$ , inclusive.
5. The heat sink as defined in claim 1 or 2, wherein the ratio of the number of atoms of the metal (B) to that of whole heat sink lies between 0.01 and 2.5 atm%, inclusive.
6. The heat sink as defined in claim 1 or 2, wherein the metal (B) comprises at least one metal selected from the group consisting of Ti, Zr, and Hf.
7. The heat sink as defined in claim 1 or 2, wherein the metal (A) comprises an alloy of Ag and Cu with the condition that  $\text{Ag} \geq 0.6$  or  $\text{Cu} \geq 0.8$  in the volume ratio between the two is fulfilled.
8. A manufacturing method to form a heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of diamond particles, the method comprising:
  - (a) putting a plurality of diamond particles in a container or mold;
  - (b) putting an alloy (C) comprising the metal (A) and the metal (B) in the container or mold together with the diamond particles at the same time or after the diamond particles are put; and
  - (c) melting the alloy (C) with heat in a vacuum or under a pressure below 1,000 atms so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') on the surface of the individual diamond particles, and the molten alloy (C) infiltrates into the gaps between the diamond particles.
9. A manufacturing method to form a heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of diamond particles, the method comprising:
  - (a) putting a plurality of diamond particles in a container or mold;
  - (b) putting an alloy (C) comprising the metal (A) and the metal (B) in the container or mold together with the diamond particles at the same time or after the diamond particles are put;
  - (c) melting the alloy (C) with heat in a vacuum or under a pressure below 1000 atms so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') on the surface of the individual diamond particle;
  - (d) evaporating a part of the alloy (C) in a vacuum; and infiltrating the metal (A), which is separately provided, in a vacuum or under a pressure below 1000 atms.
10. A manufacturing method to form a heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of diamond particles, the method comprising:
  - (a) putting a plurality of diamond particles in a container or mold;
  - (b) putting an alloy (C) comprising the metal (A) and the metal (B) together with the metal (A), which is separately provided, having a higher melting point than the alloy (C) in the container or mold together with the diamond particles at the same time or after the diamond particles are put;
  - (c) melting the alloy (C) with heat in a vacuum or under a pressure below 1000 atms so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') on the surface of the individual diamond particles; and
  - (d) melting the separately provided metal (A).

11. A manufacturing method to form a heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of diamond particles, the method comprising:

- (a) putting a plurality of diamond particles in a container or mold;
- (b) putting an alloy (C) comprising the metal (A) and the metal (B) together with the metal (A), which is separately provided, having a lower melting point than the alloy (C) in the container or mold together with the diamond particles at the same time or after the diamond particles are put;
- (c) melting the separately provided metal (A) with heat in a vacuum or under a pressure below 1000 atms; and
- (d) melting the alloy (C) so that the metal (B) released from the alloy (C) reacts with the diamond particles to form the metal carbide (B') around the diamond particles.

12. A manufacturing method to form a heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of diamond particles, the method comprising:

- (a) mixing powders of an alloy (C) comprising the metal (A) and the metal (B) with a plurality of diamond particles;
- (b) pressure forming the mixture; and
- (c) sintering the formed body at a temperature above the melting point of the alloy (C) so that the metal (B) included in the alloy (C) reacts with the diamond particles to form the metal carbide (B') around the diamond particles.

13. A manufacturing method to form a heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of diamond particles, the method comprising:

- (a) mixing powders of an alloy (C) comprising the metal (A) and the metal (B); powders of the metal (A), which is separately provided, having a higher melting point than the alloy (C); and a plurality of diamond particles;
- (b) pressure forming the mixture; and
- (c) sintering the formed body at a temperature above the melting point of the alloy (C) and below the melting point of the separately provided metal (A) so that the metal (B) included in the alloy (C) reacts with the diamond particles to form the metal carbide (B') around the diamond particles.

14. A manufacturing method to form a heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; a metal (D) of at least one metal selected from the group consisting of tungsten, molybdenum, and alloys thereof; and a plurality of diamond particles, the method comprising:

- (a) mixing powders of an alloy (C) comprising the metal (A) and the metal (B), powders of the metal (D) having a higher melting point than the alloy (C), and a plurality of diamond particles;
- (b) pressure forming the mixture; and
- (c) sintering the formed body at a temperature above the melting point of the alloy (C) and below the melting point of the metal (D) so that the metal (B) included in the alloy (C) reacts with the diamond particles to form the metal carbide (B') around the diamond particles.

15. A manufacturing method to form a heat sink for semiconductors which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; a metal carbide (B') made from a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium; and a plurality of diamond particles, the method comprising:

- (a) mixing powders of an alloy (C) comprising the metal (A) and the metal (B); powders of the metal (A), which is separately provided, having a higher melting point than the alloy (C); and a plurality of diamond particles;
- (b) pressure forming the mixture; and

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(c) sintering the formed body at a temperature above the melting point of the separately provided metal (A) so that the metal (B) included in the alloy (C) reacts with the diamond particles to form the metal carbide (B' ) around the diamond particles.

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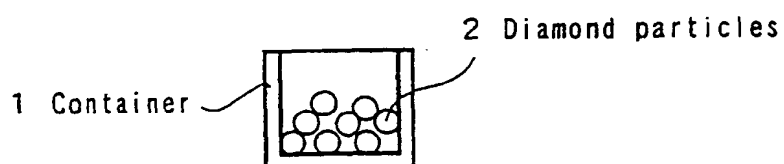
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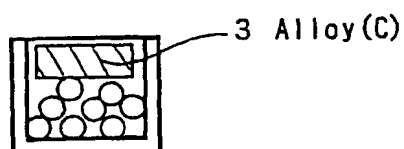
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Fig. 1

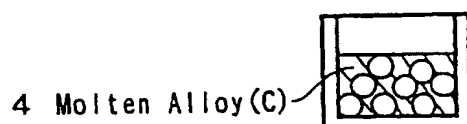
(a)



(b)



(c)



(d)

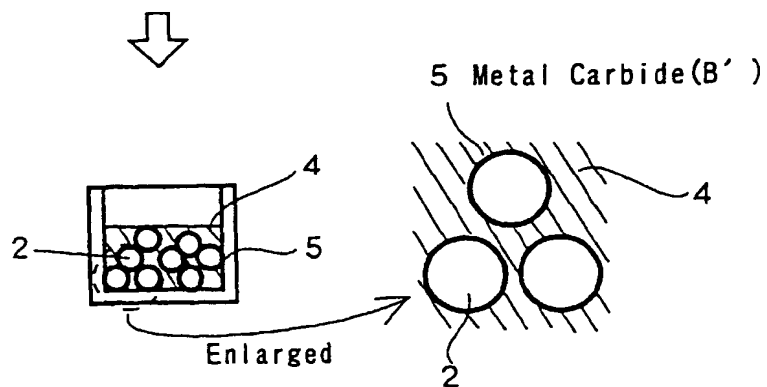


Fig. 2

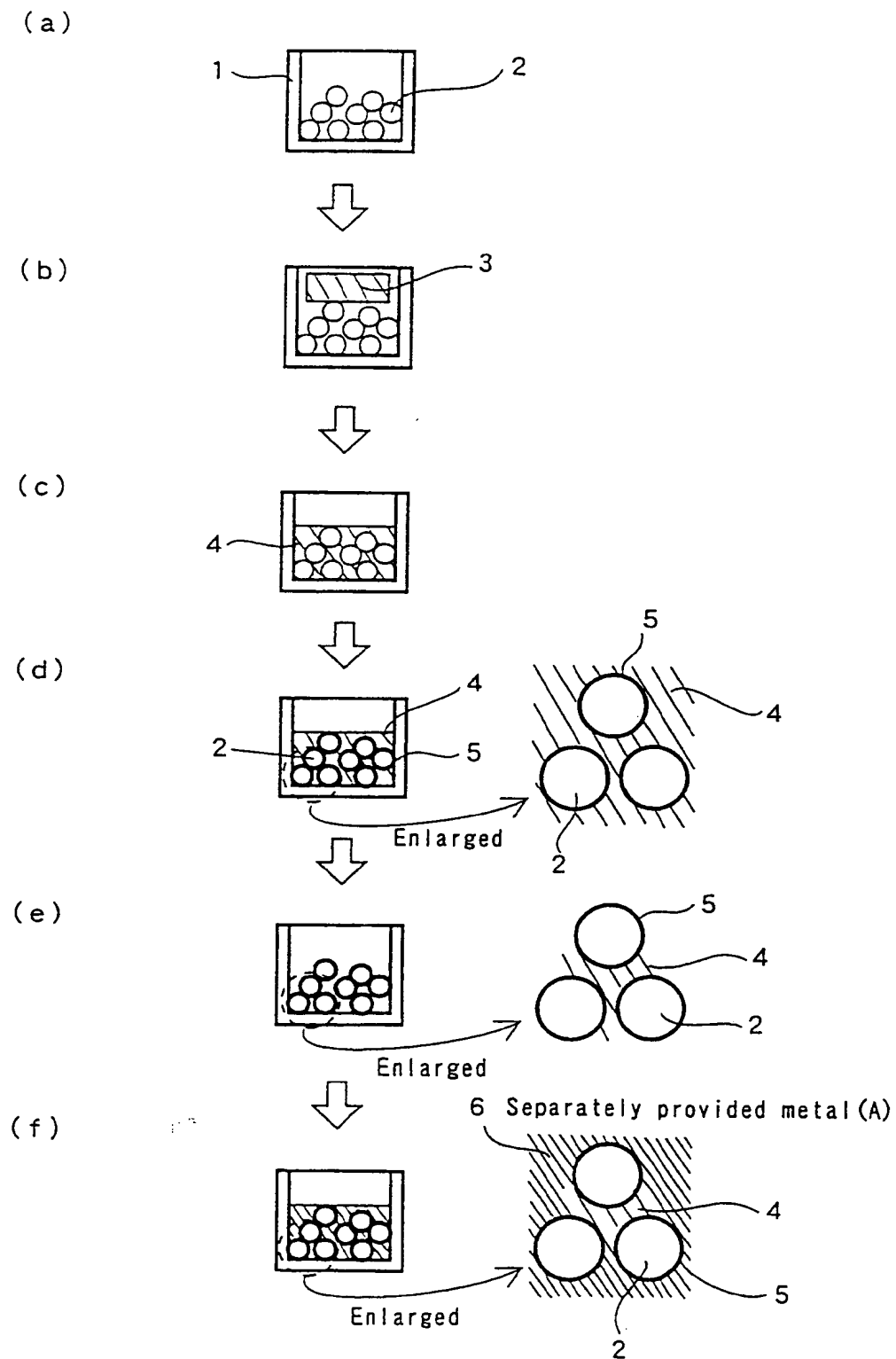
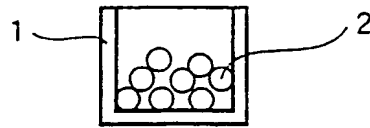


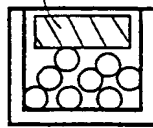
Fig. 3

(a)



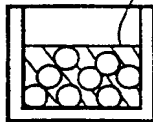
(b)

7 Separately provided metal (A)

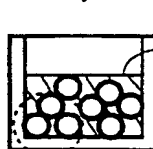


(c)

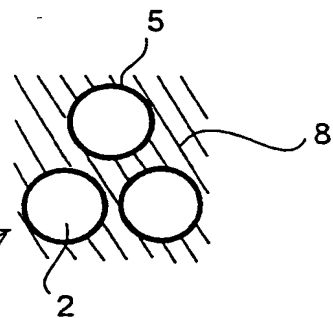
8 Two Components of molten Alloy (C) and non-molten separately provided metal (A)



(d)

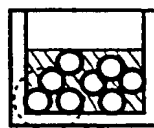


Enlarged



(e)

9 Molten Alloy (C) and molten separately provided metal (A)



Enlarged

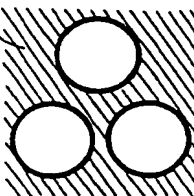


Fig. 4

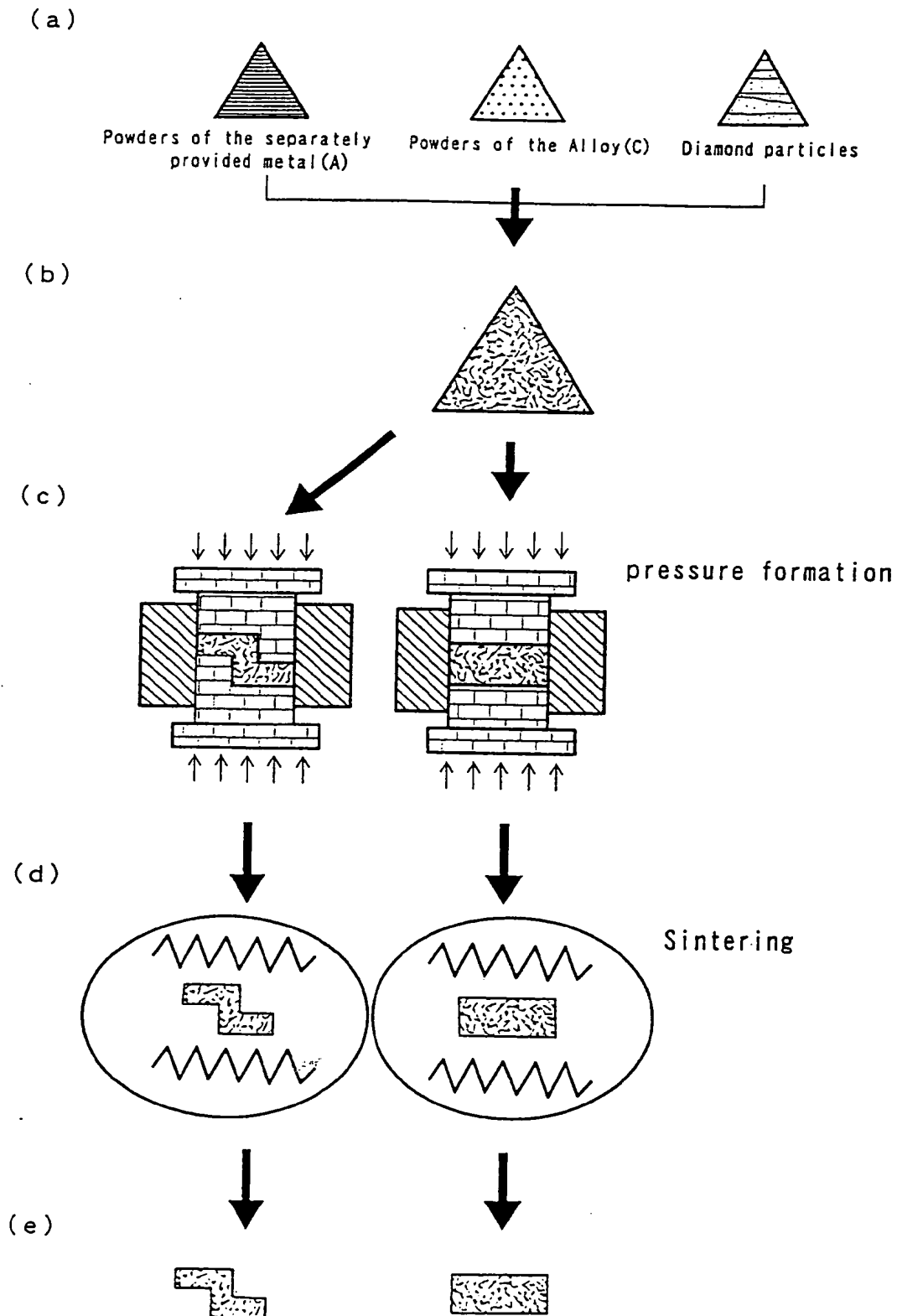


Fig. 5

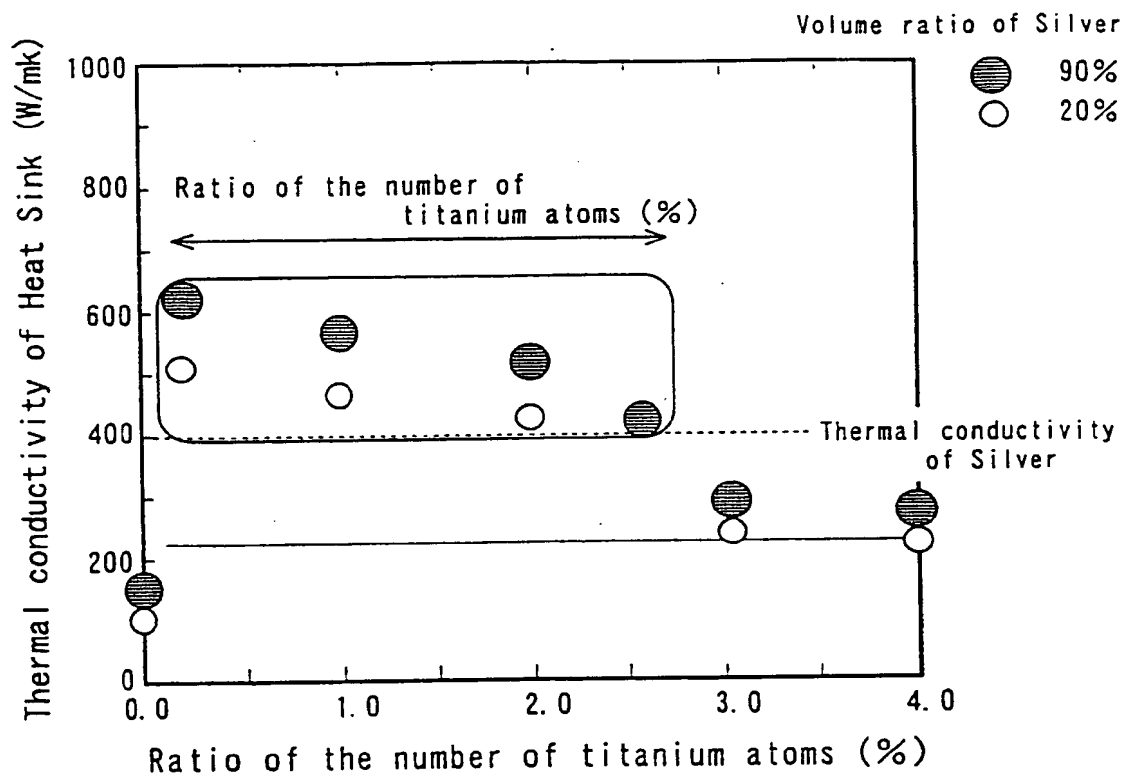


Fig. 6

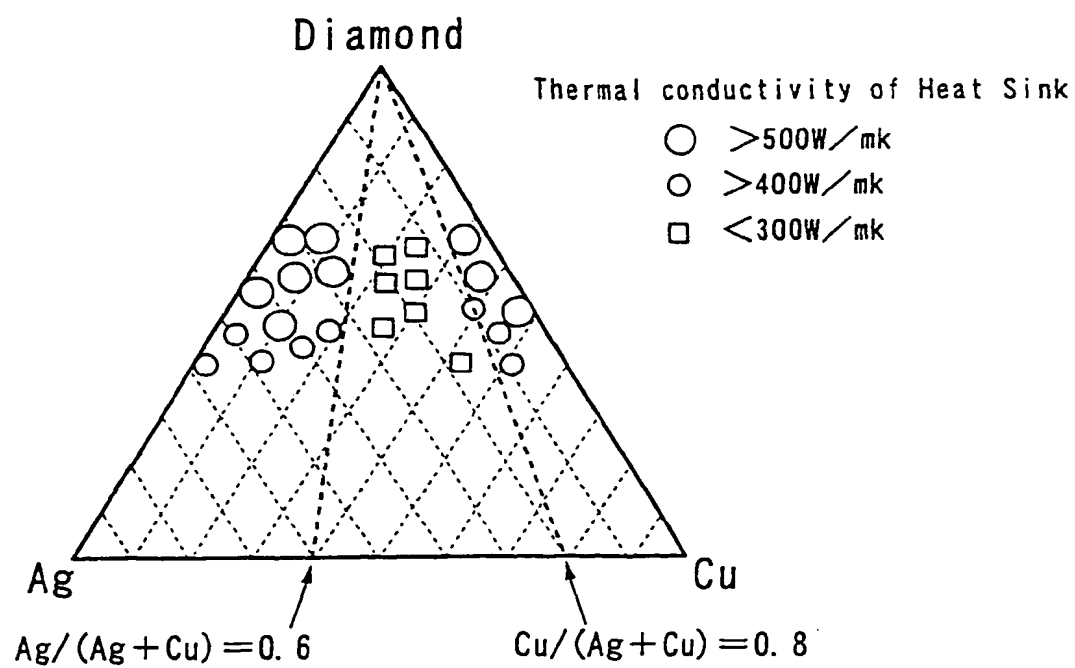
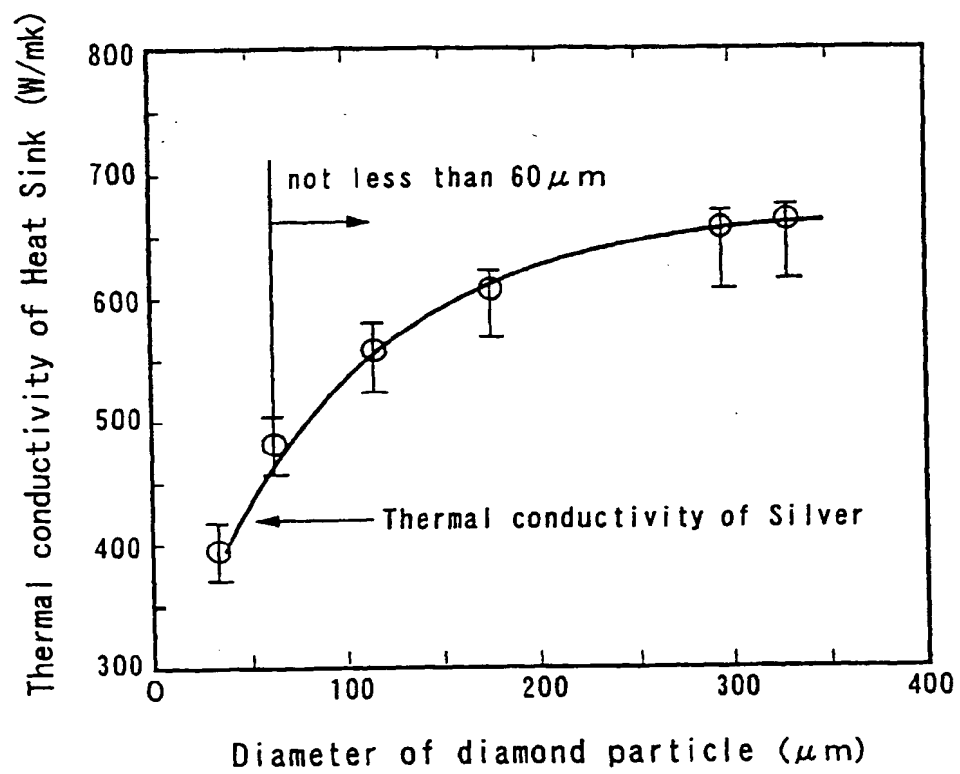
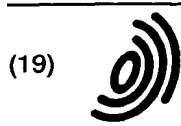


Fig. 7





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## EUROPEAN PATENT APPLICATION

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(51) Int. Cl.<sup>6</sup>: H01L 23/373

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(30) Priority: 19.08.1997 JP 22209197

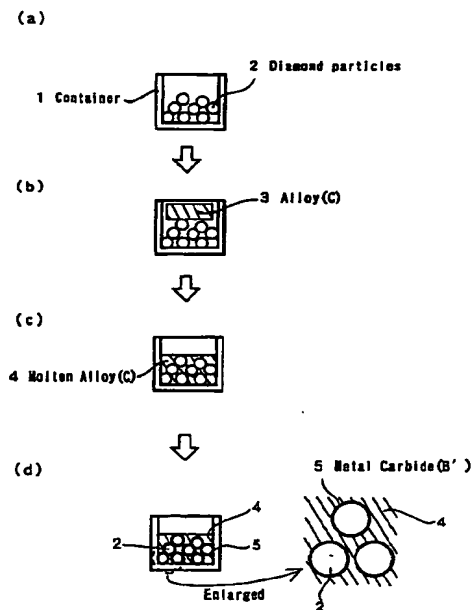
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### (54) Heat sink for semiconductors and manufacturing process thereof

(57) A highly heat conductive heat sink comprising diamond particles yet eliminating heat distortion problems caused by the difference in thermal expansion with a semiconductor, and a manufacturing method thereof. Melting of an alloy (C), which comprises a metal (A) of at least one metal selected from the group consisting of Cu, Ag, Au, Al, Mg, and Zn; and a metal (B) of at least one metal selected from the group consisting of the groups 4a and 5a of the Periodic Table and chromium, around diamond particles forms on the surface thereof a metal carbide (B'), which enables the strong bonding between the diamond particles and the metal (A) and thus produces a highly heat conductive heat sink having a much higher thermal conductivity than the metal (A). This structure is attainable by either an infiltration method or sintering method. A special feature, or effectiveness, of the invention lies in that the metal carbide (B') is formed on the surface of the diamond particles at the same time as or after the formation of a metal matrix. It is essential that not less than a quarter of the surface of the diamond particles be covered with the metal carbide (B') and the diamond particles be separated with one another by metal.

Fig. 1





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# EUROPEAN SEARCH REPORT

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| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                              |                                                     |
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| The present search report has been drawn up for all claims                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                              |                                                     |
| Place of search<br><b>THE HAGUE</b>                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                                   | Date of completion of the search<br><b>16 August 1999</b>                                                                                                                                                                                                                    | Examiner<br><b>Prohaska, G</b>                      |
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Application Number  
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| The present search report has been drawn up for all claims                                                                                                                                                                                                    |                                                                                                                                                                                     |                                                                                                                                                                                                                                                                              |                                              |
| Place of search<br><b>THE HAGUE</b>                                                                                                                                                                                                                           |                                                                                                                                                                                     | Date of completion of the search<br><b>16 August 1999</b>                                                                                                                                                                                                                    | Examiner<br><b>Prohaska, G</b>               |
| <b>CATEGORY OF CITED DOCUMENTS</b><br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |                                                                                                                                                                                     | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |                                              |

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 11 4207

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